ENGINEERING DATA FOR BLACK LIQUORS

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By
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CERTIFICATE

It is certified that this work has been carried out under my supervision and that it has not been submitted elsewhere for a degree.

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Author

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NOMENCLATURE

A_1	Surface area of the plate No.1
A_{12}	Average surface area of the liquor between the Plates 1 and 2
A_{21}	Surface area of the top portion of the plate 2
A_{22}	Surface area of the bottom face of the plate 2
A_{23}	Average surface area of the liquid between the plates 3 and 2
A_3	Surface area of the top portion of the plate 3
c	concentration of black liquor % solids
C_p	Specific heat
C_{pB}	Specific heat of black liquor
C_{pW}	Specific heat of water
C.E.	Water equivalent of calorimeter
E1, E2, E3	Emf reading of the plate 1, 2,3
I	Current (amperage)
k_1, k_2, k_3	thermal conductivity of the plates 1,2, and 3
k_c	viscometer constant
k_U	thermal conductivity of upper liquid
k_1	thermal conductivity of lower liquid
Q_{12}	Heat transfered from plate 1 to plate 2
Q_{23}	Heat transfered from plate 2 to plate 3
Q_L	Heat losses to surroundings
s	shear stress
s	specific gravity

T_{12}	Temperature difference between plate 1 and 2
T_{23}	Temperature difference between plate 2 and 3
T	Temperature in °C
T_o	Temperature after the shutting off of the heat supply.
U_{12}, U_{23}	Overall heat transfer coefficient for the upper liquid part and lower liquid part
V	Volume of the liquid taken in capillary viscometer
V_z	Velocity component along z direction
W	Weight added, weight of sample taken in specific heat apparatus
w	Angular velocity
w	Weight of water
x_1, x_2, x_3	Thickness of plates, 1,2,3
x_u	Thickness of upper liquid layer
x_l	Thickness of lower liquid layer
η	Viscosity in centi poises
η_N	Viscosity for Newtonian model
θ	Time
ρ	Density
Ω	r.p.m. of the rotor.

ABSTRACT

Engineering properties such as specific gravity, viscosity, thermal conductivity, specific heat and boiling point elevation are determined experimentally for commercial black liquor samples from pulping bamboo, bagasse and eucalyptus species. The data obtained cover the temperature range 30-95°C and 15 to 61 percent solids liquor concentration and correlating equations are developed for use in process engineering and design calculations.

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CHAPTER I

INTRODUCTION

Paper industries in India are based on the use of alkaline processes for making pulp from various indigeneous fibrous raw materials such as bamboo, grasses, bagasse, mixed hardwoods, etc. The major constituents of these raw materials are cellulose, hemicellulose and lignin, extraneous components and inorganics such as silica are present in small quantities. The chemical composition of some of these species are shown in Table 1-1.[1]

The pulping process consists in treating the fibrous raw materials with white liquor-sodium hydroxide (soda process) or sodium hydroxide and sodium sulfide (sulfate or kraft process) at 160-180°C. The pulping chemicals cause the degradation and dissolution of the non-cellulosic portions. The spent liquor from pulping, termed as black liquor, is a complex mixture of organic and inorganic chemicals. The organic compounds include low molecular weight alkali lignin and thiolignin, sugar residues as isosaccharinic acids, low molecular weight polysaccharicles and extraneous compounds such as resin and fatty acids. These organic compounds are present mostly as sodium salts. The inorganic chemicals in black liquor include sodium hydroxide, sodium sulfide, sodium carbonate and small amounts of sodium sulfate, sodium thiosulfate

etc. depending upon make up chemical used and recycle practices. Silica from bamboo, bagasse and grasses enters the black liquor as sodium silicate. The proportion of organic compounds in the black liquor is in the range 50-70 percent depending upon the chemical composition of the species used, digester operating conditions and pulp yield.

The weak black liquor after digestion and washing steps is at 50-90°C with a pH of 10.5-13.0 and 12-25 percent dissolved solids concentration. This weak liquor is concentrated to 50-55 percent solids in multiple effect evaporators (4 to 7 effects). A flue gas contact evaporator is commonly used for further evaporation to a concentration of about 64 percent solids, suitable for self-sustained combustion in the recovery boiler. The inorganic chemicals in black liquor are recovered as sodium carbonate and sodium sulfide smelt in the reducing atmosphere of the recovery furnace. The fuel value of the reduced organic compounds is realized in the oxidation zone of the recovery boiler and utilized for producing steam for mill use and power generation. White liquor for reuse in the pulp mill is prepared from smelt chemicals by causticization.

The recovery of pulping chemicals is necessary for an economical operation of the alkaline pulp mill. Efficient and continuous operation of the evaporators and recovery furnace depend upon the characteristics of the solids present in the black liquor. This work deals with fundamental engineering

data of black liquors from pulping of indigeneous fibrous raw materials.

The physical properties of black liquors are necessary for the design and operation of the chemical recovery units. They are also necessary for process development work and scale-up studies of laboratory and pilot plant results. The use of reliable and accurate values of the physical properties of black liquors would ensure an efficient and economic design of process equipment. The properties included in this investigation would comprise of specific gravity, viscosity and rheological behavior, thermal conductivity specific heat and boiling point elevation. Several of the procedures available for estimating the above properties are suitable for pure compounds and simple mixture.(2) The applicability of such techniques to the complex black liquor from the pulp mill is not known with certainty. Harvin(3) has correlated the specific gravity, viscosity, thermal conductivity and specific heat of pine black liquor with concentration and temperature. Han(4) has studied the physical properties of neutral sulphite spent liquor from pulping of western hemlock. Kobe and McKormack(5) have reported the viscosity data for various black liquors. Physical properties of black liquors from pulping indigeneous fibrous raw materials such as bamboo, bagasse, etc. are not readily available in published literature.

Experimental data for the specific gravity, viscosity, thermal conductivity, and specific heat are correlated with temperature and solids concentration for various black liquors. Non Newtonian behavior of the black liquor at higher concentration is also investigated. Experimentally determined values of such properties would be reliable for use in process design calculations.

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TABLE 1-1: CHEMICAL COMPOSITION OF FIBROUS RAW MATERIALS (PERCENT)(1)

Constituent	Bamboo	Bagasse	Eucalyptus Hybrid.
Ash	3.19	1.77	0.44
Silica	1.40	1.40	0.03
1% NaOH solubility	28.30	30.23	13.40
Pentosans	19.30	24.10	14.10
Alcohol-benzene extraction	4.19	1.90	1.48
Lignin	24.15	19.37	30.90
Holocellulose	67.19	73.16	65.80
Alphacellulose	46.58	41.94	45.1

CHAPTER II

SPECIFIC GRAVITY OF BLACK LIQUORS

A knowledge of the specific gravity of black liquors is necessary for process engineering calculations dealing with chemical recovery operations of a kraft pulp mill. Compilation of specific gravity data in the literature[3,4] deals mainly with black liquors from the pulping of softwoods. Specific gravity data for spent liquors from the pulping of bamboo, bagasse an other agricultural resues are not readily available.

In this investigation specific gravities are determined for commercial samples of bamboo, bamboo + salai (10%), bagasse and eucalyptus black liquors having organic and inorganic ratios shown in Table 2-7. Specific gravity determinations were made using a hydrometer and a constant temperature bath temperature controlled to an accuracy of $\pm$ 0.05°C. Data are obtained for the temperature range 30-90°C and black liquor concentration range 15-55 percent total solids.

The specific gravity results for black liquors from pulping bamboo, bamboo + salai, bagasse and eucalyptus species are presented in Tables 2-1 to 2-4 respectively. Specific gravity results are graphically correlated with concentration in Figures 2-1 to 2-4 using temperature as the parameter.

An empirical equation was fitted to the data with the help of computer calculation by the least square curve fitting method. The general form of the equation obtained is represented

by Equation 2-1.

$$s = (a_1 + a_2c) + (a_3 + a_4c)T \qquad (2\text{-}1)$$

where a_1, a_2, a_3, and a_4 are constants. The values of these constants for the black liquor samples used in this work are given in Table 2-5. Equation 2-1 fits the experimental data within 1 percent error, for all the liquor samples.

The graphs in Figures 2-1 to 2-4 show that the specific gravity varies linearly with concentration at a constant temperature for all the black liquors samples of this investigation. Similar behavior has been reported by Harvin(3) and Han.(4)

The graphs in Figure 2-5 gives a comparison of the specific gravity at 70°C for the various black liquors samples used in this work. The specific gravity values increase in the order bagasse, bamboo and eucalyptus black liquors. However, the differences in specific gravities are rather small within 2 percent for all liquors.

Table 2-6 shows a comparison of specific gravity of black liquors from laboratory and commercial scale pulping of eucalyptus. These values differ by less than 2.5 percent and hence the data of Table 2-4 and Figure 2-4 for eucalyptus black liquors from laboratory pulping would be adequate for process engineering calculations.

The general Equation fitted to all the experimental data

was

$$s = (1.0104939 + 0.00755064c) + (-0.00043592 + 0.0000441c)T \quad (2\text{-}2)$$

Equation 2-2 may be used to fit all the specific gravity data of this work with the values of constants shown in Table with an error less than 2.0 percent. Table 2-8 shows the values of specific gravity for concentration range of 20-60 % solids and temperature range of 30-100°C for black liquors based on Equation 2-2. The values generalized correlation for the specific gravity of black liquors given here may be used for process calculation.

TABLE 2-1: SPECIFIC GRAVITY OF BAMBOO BLACK LIQUOR

Temp., °C	Percent Solids			
	13.50	26.50	38.00	54.00
20	1.102	1.212	1.289	1.416
50	1.096	1.194	1.279	1.404
70	1.086	1.180	1.262	1.382
90	1.072	1.167	1.250	1.368

TABLE 2-2: SPECIFIC GRAVITY OF BAMBOO+SALAI BLACK LIQUOR

Temp., °C	Percent Solids			
	14.00	24.5	44.00	60.00
20	1.1040	1.178	1.324	1.440
50	1.0880	1.161	1.302	1.1417
70	1.0780	1.154	1.288	1.4000
90	1.0680	1.114	1.275	1.3880

TABLE 2-3: SPECIFIC GRAVITY OF BAGASSE BLACK LIQUOR

Temp., °C	Percent Solids			
	14.5	27.5	45.0	50.0
30	1.099	1.190	1.340	1.348
50	1.088	1.178	1.300	1.334
70	1.076	1.166	1.288	1.324
90	1.068	1.156	1.271	1.312

TABLE 2-4: SPECIFIC GRAVITY OF EUCALYPTUS BLACK LIQUOR

Temp., °C	Percent Solids			
	12.5	28.0	55.0	42.0
35	1.092	1.218	1.428	1.326
50	1.087	1.208	1.418	1.318
70	1.076	1.196	1.408	1.306
90	1.065	1.185	1.386	1.295

TABLE 2-5: CONSTANTS OF EQUATION 2-1 FOR VARIOUS BLACK LIQUORS

Black Liquor	a_1	$a_2 \times 10^2$	$a_3 \times 10^3$	$a_4 \times 10^5$
Bamboo	1.0182	.779	-.219	.321
Bamboo + Salai(10%)	1.0168	.753	-.239	-.311
Eucalyptus	1.0181	.815	-.243	-.266
Bagasse	1.0207	.712	-.279	-.117
General	1.0105	.755	-.436	-.441

$$s=(a_1+a_2c) + (a_3+a_4c)T \qquad (2-1)$$

where c is in in percent solids, T in °C

TABLE 2-6: COMPARISON OF SPECIFIC GRAVITY OF BLACK LIQUOR FROM LABORATORY AND COMMERCIAL PULPING OF EUCALYPTUS

Percent Solids = 12.5

Temperature, °C	Specific gravity Commercial	Specific gravity Laboratory*	Percent Difference
35	1.065	1.093	2.56
50	1.0575	1.085	2.53
70	1.0475	1.075	2.56
90	1.0375	1.065	2.58

*Extrapolated values based on Fig. 2-4

TABLE 2-7: PROPORTION OF ORGANIC AND INORGANIC COMPOUNDS IN BLACK LIQUOR SOLIDS

Black Liquors	% Organic	%Inorganic
1. Bamboo	61.30	38.7
2. Bamboo+ Salai	58.15	41.85
3. Eucalyptus	59.40	40.60
4. Bagasse	51.00	49.00

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TABLE 2.8: SPECIFIC GRAVITY OF BLACK LIQUORS*

Temp., °C	Percent Solids				
	20	30	40	50	60
30	1.146	1.220	1.294	1.368	1.442
40	1.141	1.215	1.289	1.363	1.437
50	1.136	1.210	1.283	1.357	1.430
60	1.131	1.204	1.277	1.350	1.423
70	1.126	1.198	1.271	1.343	1.416
80	1.120	1.192	1.264	1.336	1.408
90	1.113	1.185	1.256	1.327	1.399
100	1.107	1.178	1.248	1.319	1.389

*Based on Equation 2-2

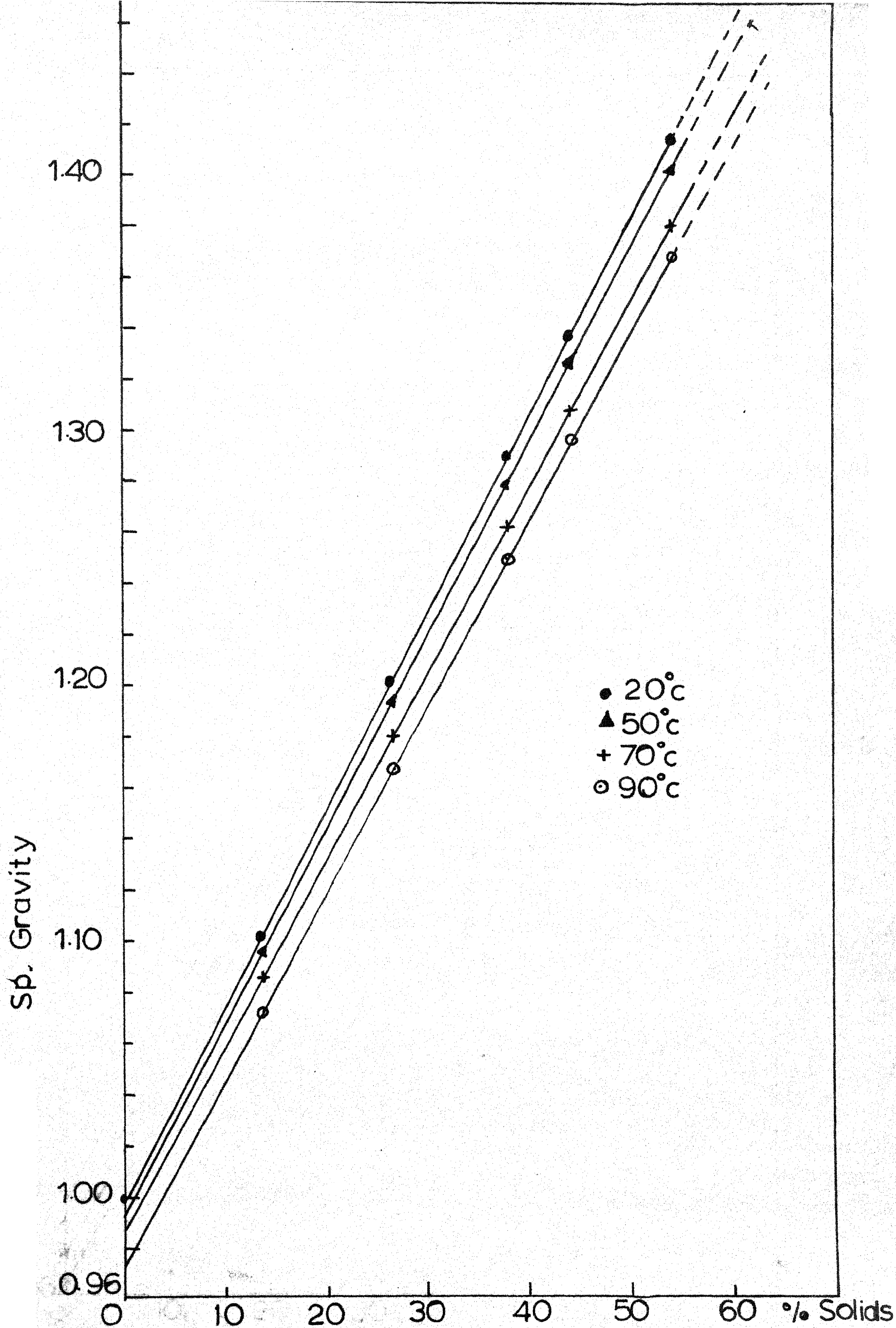


Fig. 2-1 Specific gravity of bamboo black liquor

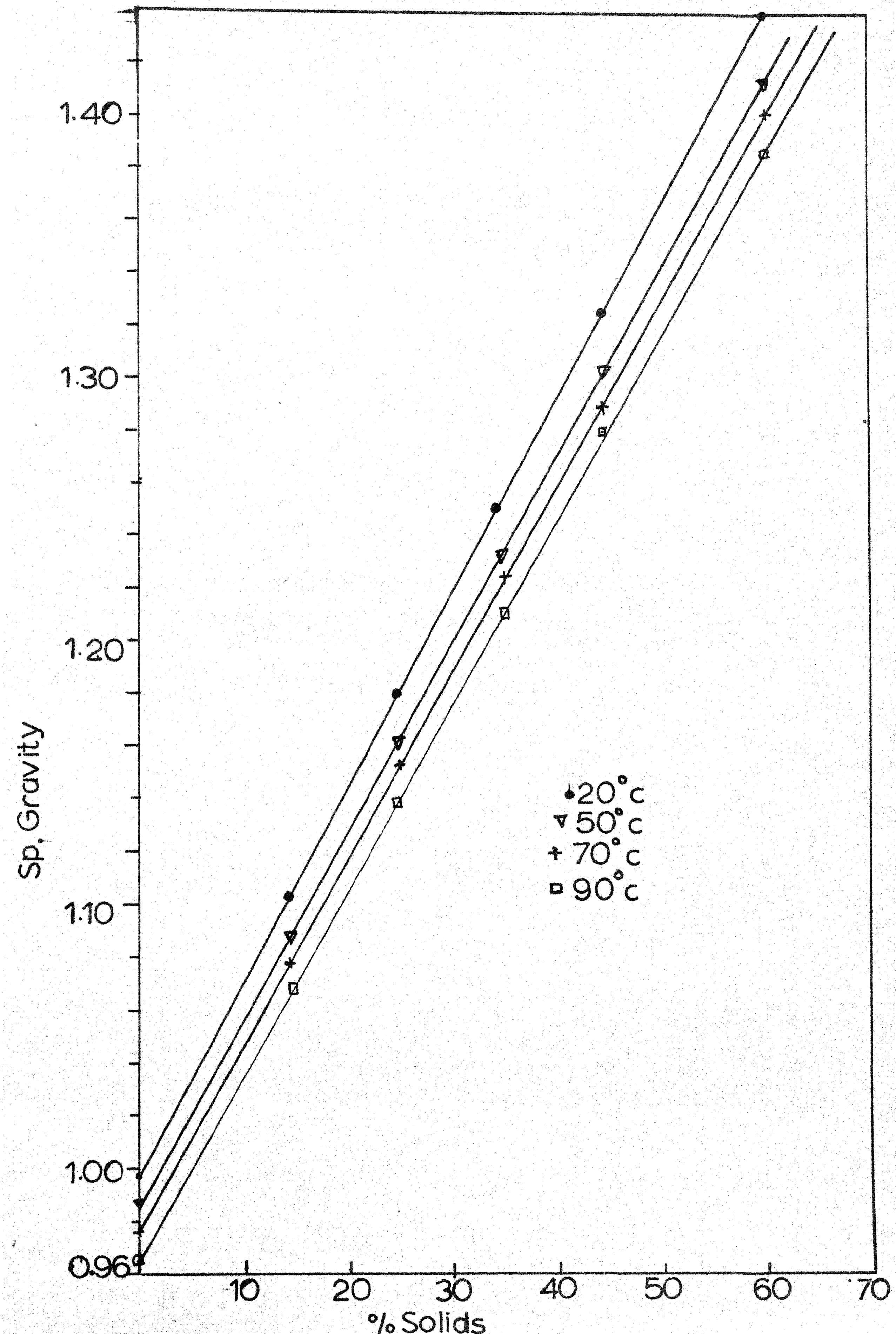


Fig. 2-2 Specific gravity of bamboo(90%) + salai(10%) black liquor

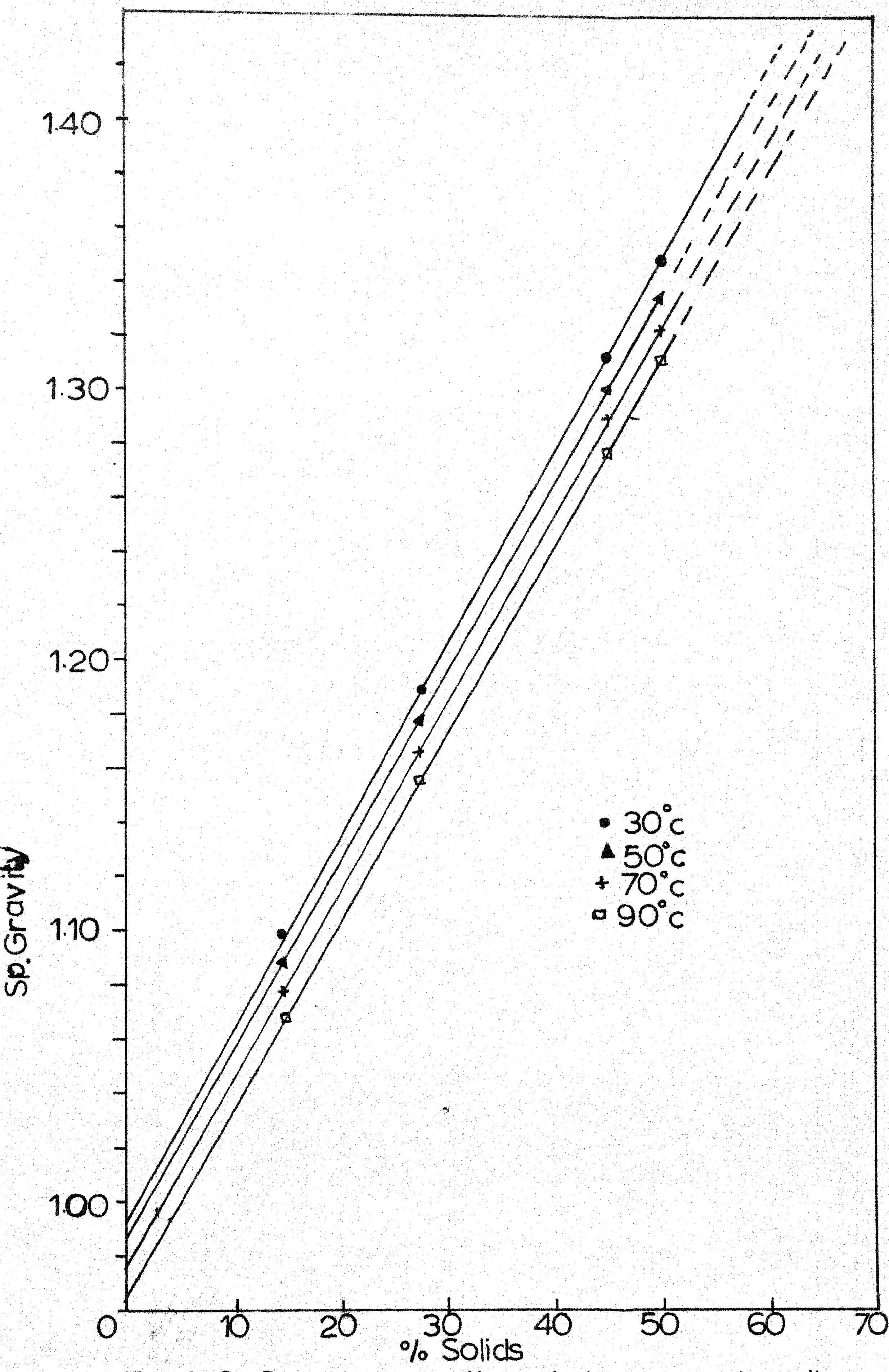


Fig. 2-3 Specific gravity of bagasse black liquor

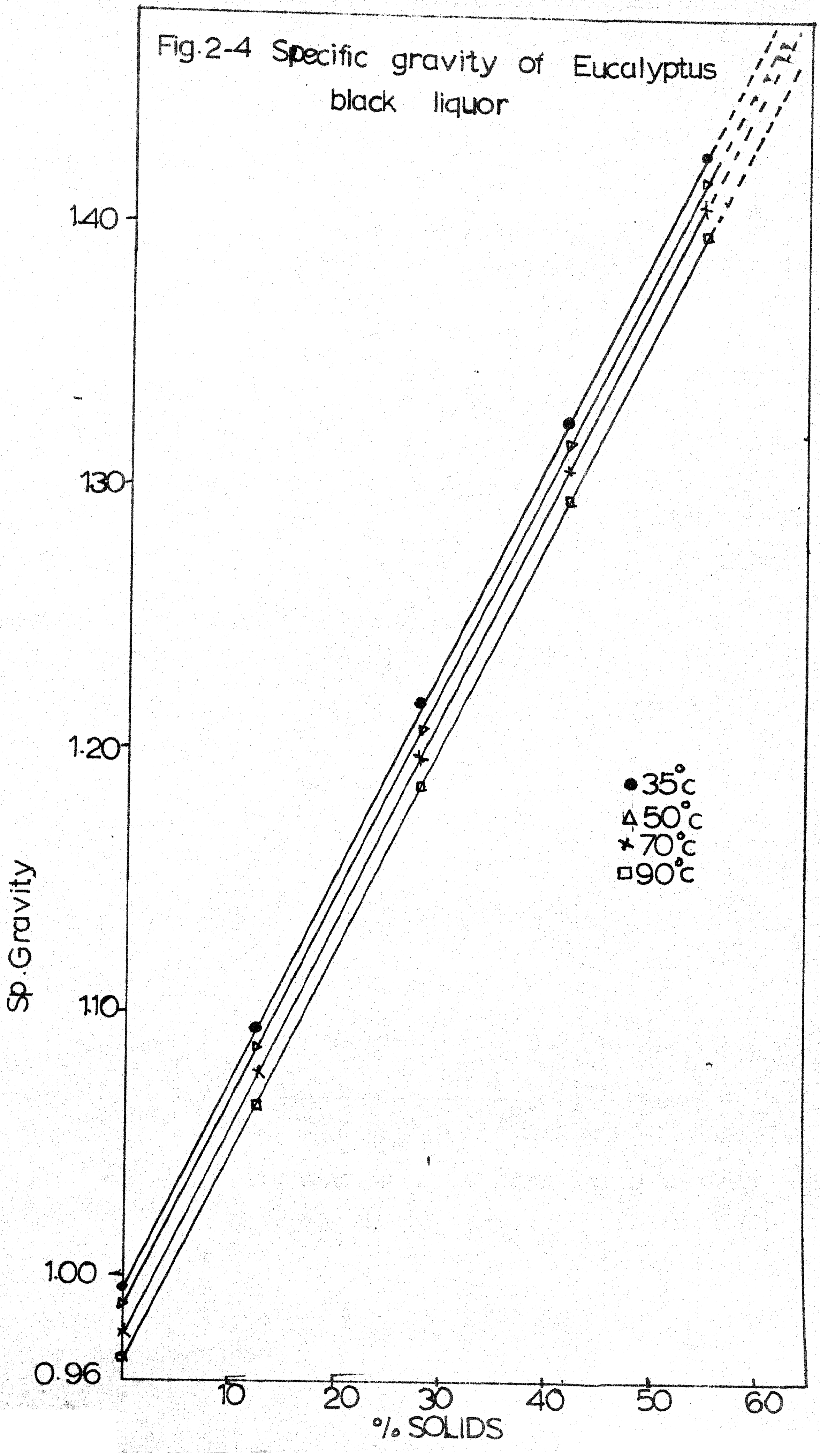


Fig. 2-4 Specific gravity of Eucalyptus black liquor
1.40
1.30
1.20
1.10
1.00
0.96
Sp. Gravity
10
20
30
40
50
60
% SOLIDS
● 35°c
△ 50°c
✶ 70°c
□ 90°c

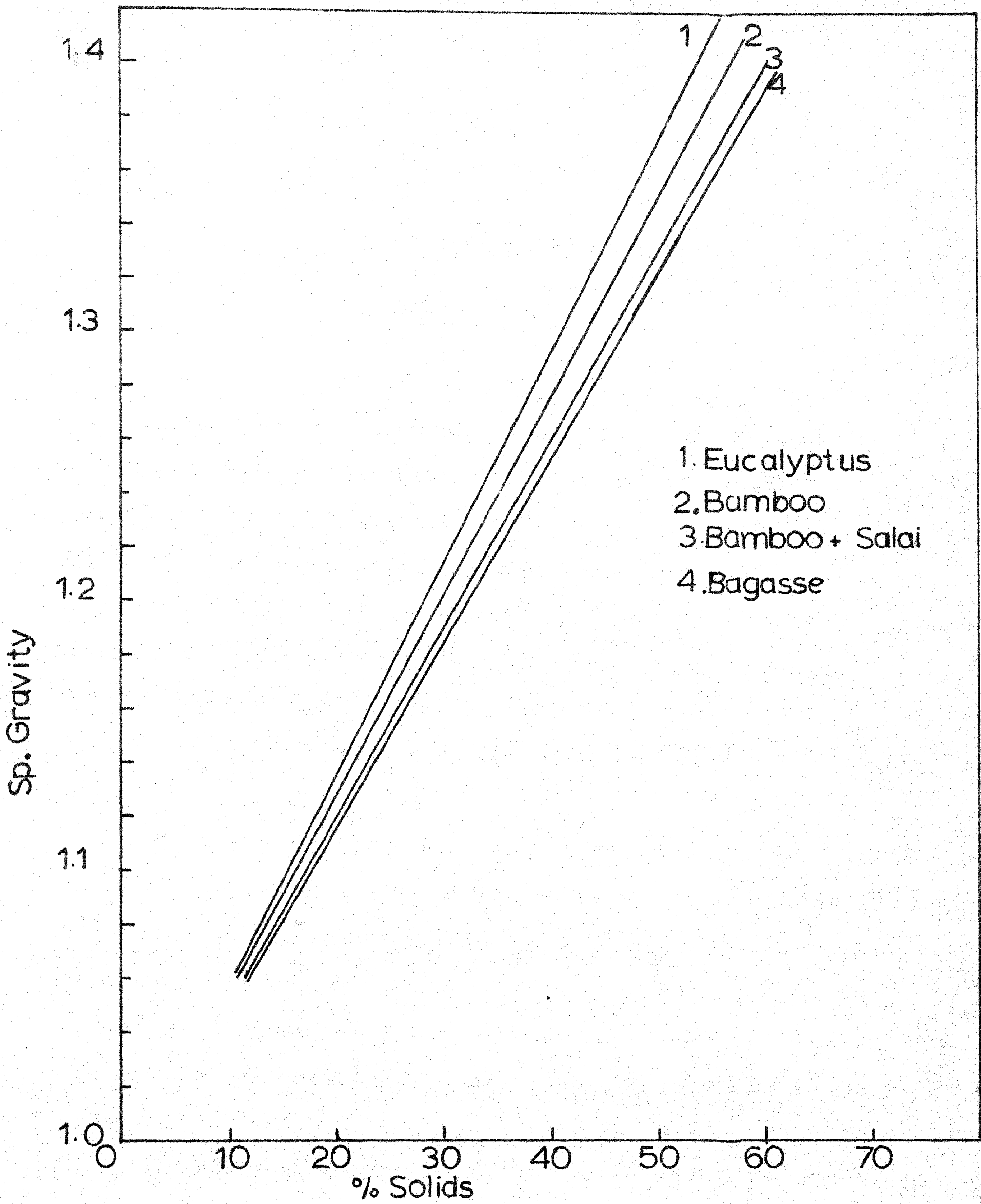


Fig. 2-5 Comparision of specific gravities of various black liquors

CHAPTER III

VISCOSITY OF BLACK LIQUORS

Viscosity is one of the more important properties of black liqurs used in the selection and design of equipments and process engineering calculations of chemical recovery operations of a kraft pulp mill. Viscosity of black liquor varies with changes in concentration and temperature. The organic constituents of the black liquor such as dissolved lignin, hemicellulose and other carbohydrates contribute largely to the viscosity of the solution. Thus the viscosity of black liquor may be expected to vary also with species, pulping condition and pulp yields.

The viscosity increases considerably especially at higher concentration levels and could adversely affect satisfactory operations of evaporators and decrease the heat transfer rates. Viscosity is an important factor in the selection of pumps and the design of spray nozzles for the recovery boiler. Power requirements are considerably greater for pumping viscous black liquors.

The correlation of viscosity with respect to temperatures and concentration is needed for calculating the Reynolds and Prandtl numbers in order to estimate the heat transfer coefficient in evaporators.

Viscosity is the resistance offered by the fluid for its flow. Ideal viscous bodies exhibit flow with the rate of flow being function of stress and cannot sustain strains for long since these are relieved by flow. The coefficient of viscosity or viscosity is t· ratio of applied shearing stress to the rate of shear.

The best known ideal viscous body is Newtonian fluid for which the coefficient of viscosity is constant. The so called kinematic viscosity is directly observed in capillary tube viscometers where the stress comes from the head of the liquid. Reciprocal of viscosity is termed fluidity. The viscosity of non-Newtonian fluids varies by several orders of magnitude with changing rate of shear. Details of various types of non-Newtonian fluids are discussed by Van Wazer and Lyons.[6]

Theoretical prediction of viscosity of electrolytic solution is dealt in detail by Stokes and Mills[7]. The viscosity of an electrolytic solution can be given by Equation 3-1.

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc \qquad (3\text{-}1)$$

where, η, η_o - viscosities of the solvent and solution respectively. in centi poise

c - concentration of the solute

A, B - constants determined by knowing the ionic interactions and molecular properties.

Values of A have been calculated for various compounds but for values of B experimental determination of viscosity is done and plotting a graph of ($\frac{\eta}{\eta_0}$ - 1)/$\sqrt{c}$ versus $\sqrt{c}$ gives the slope as the values of B. No satisfactory theoretical prediction has been possible for the va es of B. Values of A and B have been given in [7,8] for various compounds such as sodium chloride, sodium sulphate, etc. A theoretical model can be developed for estimating the viscosity of simple solutions of various compounds by using mixing rules.[9] But in case of black liquor through the analysis of inorganic compounds is possible, but that of organic compounds is difficult. Hence the complexity of the black liquor makes the theoretical prediction difficult and necessitates experimental techniques.

Viscosity of black liquors has been investigated by Kobe and Mc Cormack[5], Hedlund[10] and Harvin[3]. Han[4] the viscosity of neutral sulphite liquors. Kobe and McCormack[5] using a capillary viscometer studied effects of temperature and concentration on viscosity of sulphite, sulphate and soda spent liquors from pulping of western Hemlock. Harvin[3] has correlated the viscosity of pine liquors with temperature and concentration. Han[4] has correlated the viscosity of the neutral sulphite spent liquor from various mills and also studied their non-Newtonian behavior at higher concentration using capillary and Brookfield viscometers. He suggested Equation 3-2 for the apparent viscosity of neutral sulphite, spent liquor.

$$\eta = \eta^{o} + \theta/\sigma \qquad (3\text{-}2)$$

where η^{o} - the residual viscosity,

θ - the coefficient of thixotropy,

σ - the rate of shear.

His study indicated that neutral sulphite spent liquors behaved thixotropically above 47% solids concentration.

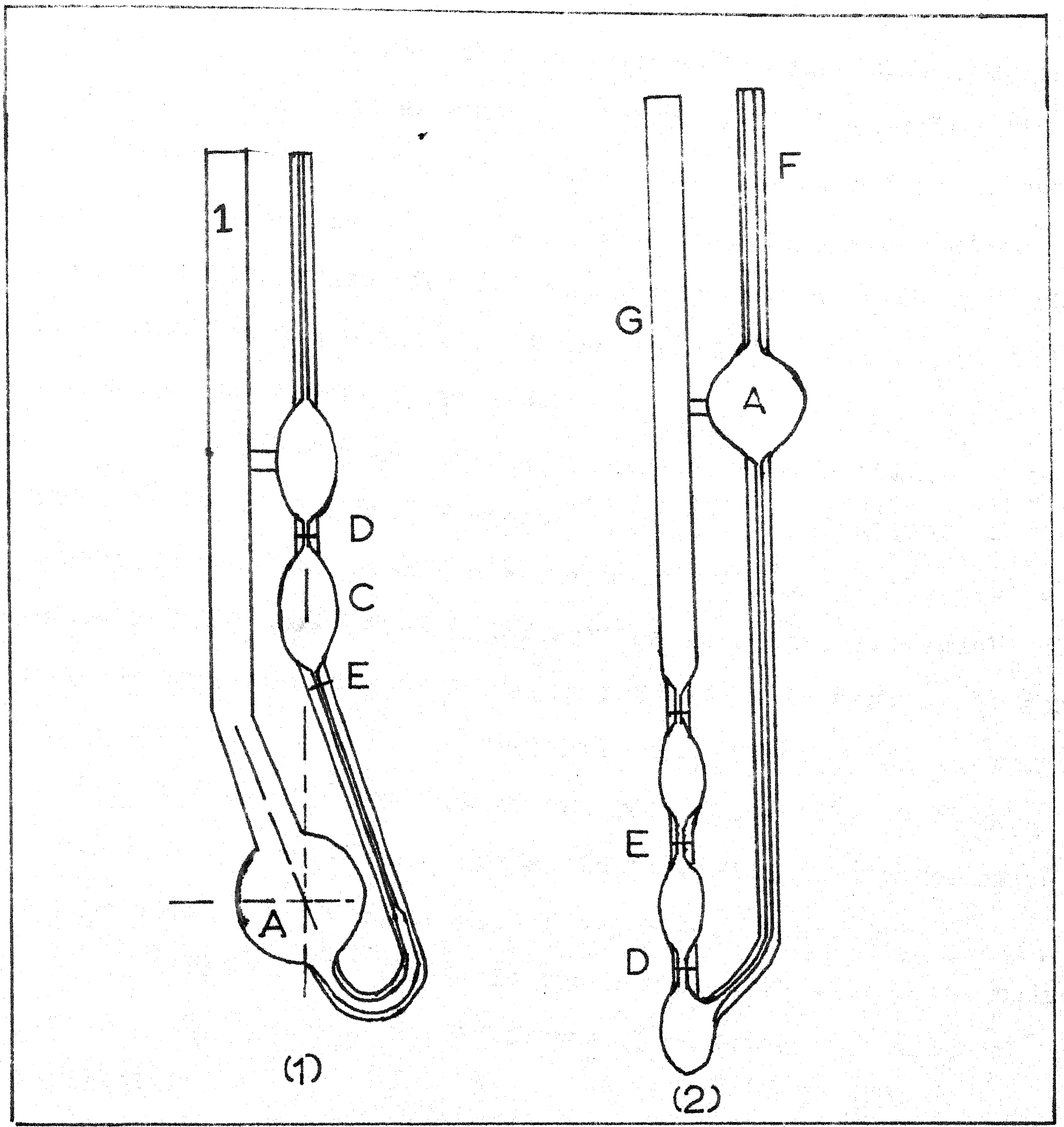
Present work deals with the determination of viscosity of various commercial black liquors from kraft pulping, bamboo bagasse, and bamboo+salai wood and eucalyptus species. Non-Newtonian behavior of some of the black liquors has been studied at higher concentrations. Cannon Fensky viscometer was used upto 30% solids, modified Cannon Fensky Viscometer upto 40% solids, and Stormer viscometer was found suitable above 40% solid concentration.

Capillary Viscometer

THEORY

Capillary Viscometer: Most of the capillary viscometers are operated by the force of gravity only. This is used for low viscosities starting from 0.4 to 160000 c.s. Rheology of non-Newtonian liquids can also be studied using external pressure techniques. Shear stress in capillary viscometer is of the order of 10-150 dynes/cm.^{2} under gravity and the rate of shear ranges from 1-20000 sec^{-1} based on 200-800 sec efflux time.

The principle of the capillary viscometers is derived from the viscometer originally used by Ostwald. Basically



Cannon Fenske Viscometers

Fig 3-a 1.For transparent liquids

2.For opaque liquids

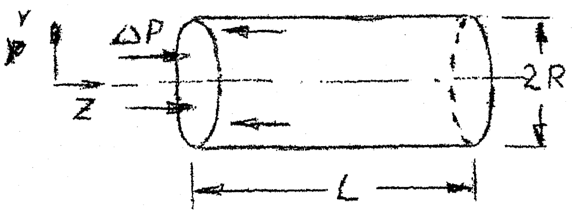
the viscometer consists of reservoir bulbs and a capillary in a U tube arrangement as shown in Figure 3-1. The efflux time of a fixed volume of liquid under an exactly reproducible mean hydrostatic head is measured. Glass capillary viscometers have been widely used for determining the viscosities of Newtonian liquids and gases because of their excellent accuracy, relative cheapness and simple operation.

Theory of glass capillary viscometers is available in standard books on fluid dynamics.[11,12,13] Derivations of equations are done with the assumption of(a)steady flow (b) absence of radial and tangential components of velocity, (c) axial velocity being a function of distance from the axis alone, (d) absence of slipage at the wall (e) negligble and effects, (f) in compressibility of fluid (g) absence of external forces (h) isothermal conditions (i) neglecting change in viscosity due to pressure change along the short length of the tube.

Considering a fluid in laminar flow in a tube of radius R. length L with a pressure difference ΔP between the ends of the capillary.

Viscous force $= s.A = s.\,(2\pi rL)$

The applied force tending to move the cylindrical column in the direction of flow is $\Delta P\,\pi r^2$. At steady state these forces should be equal, giving



$$s.2\pi rL = \Delta P\,\pi r^2 \qquad (3\text{-}3)$$

or $$s = \frac{\Delta P r}{2L} \tag{3-3}$$

where s is the shear stress at the capillary wall.

For Newtonian liquids,

$$\eta = s / \left(-\frac{dv_z}{dr}\right) \tag{3-4}$$

Substituting for s,

$$\eta = \frac{\Delta P r}{2L\left(-\frac{dv_z}{dr}\right)} \tag{3-5}$$

$$-\left(\frac{dv_z}{dr}\right) = \frac{\Delta P}{2}\frac{r}{L} \tag{3-6}$$

With a boundary condition of v=0 at r = R, integration of Equation 3-6 gives the parabolic distribution of velocity, Equation 3-7.

$$v_z(r) = \frac{P R^2}{4 \eta L}\left(1 - \left(\frac{r}{R}\right)^2\right) \tag{3-7}$$

$$Q = \int_0^r v(r)\, 2\pi r\, dr = \frac{\pi R^4 \Delta P}{8 \eta L} \tag{3-8}$$

$$\frac{V}{\theta} = \frac{\pi R^4 \Delta P}{8 \eta L} = \frac{\pi R^4 \rho g h}{8 \eta L} \tag{3-9}$$

$$\eta = \frac{\theta \pi R^4 \rho g h}{8 V L} \tag{3-10}$$

or $$\frac{\eta}{\rho} = k_c \theta \tag{3-11}$$

where k_c is constant.

Equation 3-11 may be used for determing the viscosity of black liquors by the capillary method.

For accurate measurements of viscosity,kinetic energy correction, viscous and effects correction are recommended.[6]

Equation 3-3 represents the shear stress at the wall. Hence shear stress can be varied either by applying external pressure or by changing the diameter of the capillary since the length L is usually fixed (ASTM standards).

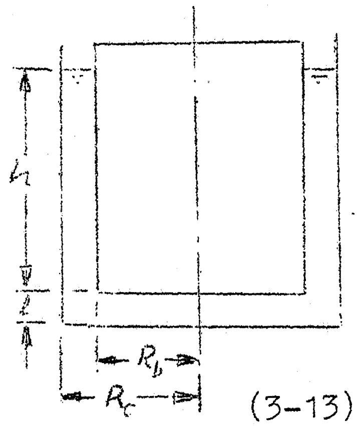
Stormer Viscometer:

Stormer viscometer is one of the few instruments in which the shearing stress is held constant rather than rate of shear.

The shear stress is applied by attaching weights to the string and permitting free fall through a vertical distance of about 100 cm. The stress may be varied by changing the weights. Stress is applied to the transmission at a winding drum on top of the housing, and then to the rotor. The gear ratio is usually 11:1. A properly maintained instrument will turn in air with about 1-2 gm. on the string. Maximum loading is about 2000 gm. without special strengthening of the frame.

The rotor is a hollow one with perforated top. Cup is placed in an open cup holder which was modified for circulation of water at constant temperature from a temperature controlled bath with an accuracy of $\pm$ 0.01°C. The cup is provided with side baffles and a central baffle which project upwards inside the rotor. The gap between the rotor and the

baffle is small (0.18 cm.) compared to 0.83 cm. between the cup wall and the rotor.



The relation between the stress and the rate of the shear for the Newtonian fluids is

$$s = \eta_N \left(- \frac{dv}{dr}\right) = \eta_N \left(-r \frac{dw}{dr}\right) \qquad (3\text{-}12)$$

$$\text{Torque} \quad M = 2\pi r^2 h \left(-r \frac{dw}{dr}\right) \eta_N \qquad (3\text{-}13)$$

$$\text{or} \quad -dw = (M/2\pi h\ \eta_N) \frac{dr}{r^3} \qquad (3\text{-}14)$$

Integrating with boundary conditions $w = 0$ at $r = Rc$ and $w = \Omega$ at $r = Rb$.

gives

$$\eta_N = \frac{M}{4\pi h \Omega}\left(\frac{1}{Rb^2} - \frac{1}{Rc^2}\right) \qquad (3\text{-}15)$$

$$\text{i.e.} \quad \eta_N = \frac{k\ M}{\Omega} \qquad (3\text{-}16)$$

where k is the constant of proportionality.

$$M \text{ for Stormer viscometer} = R \text{ drum} \times W \times g \qquad (3\text{-}17)$$

$$M \text{ rotor} = \frac{R \text{ drum} \times W \times g}{\text{gear ratio}} = k_1 W \qquad (3\text{-}18)$$

$$\therefore \quad \eta_N = \frac{k_2\ W}{\Omega} \qquad (3\text{-}19)$$

where k_2 is a constant.

$$\text{Rate of shear} = (-2\ \ /r^2)\left(\frac{Rb^2}{Rc^2}\right)/(Rc^2 - Rb^2) \qquad (3\text{-}20)$$

$$\text{shear stress } s = \frac{M}{2\pi r^2 h} = \frac{k_1\ W}{2\pi r^2 h} = k_3 W \qquad (3\text{-}21)$$

The presence of baffles and the central projection in the

cup makes the fluid flow pattern complicated and the above simple theoretical equations cannot be satisfactorily applied. Calibration of the viscometer was done by using standard glycerol solution and a graph of viscosity versus time for 100 revolution of rotor for fixed weights was drawn and it was found that the curves obtained were straight lines with a slope equal to W/A. Where A was a constant equal to 30.8 and W was weights applied(gm) and viscosity was expressed in centipoises. Hence for Newtonian liquids a general formula Equation 3-22 was for the Stormer viscometer, similar to equation 3-19

$$\eta = \frac{W \times T}{A} \qquad (3\text{-}22)$$

where T = time for 100 revolutions.

Non-Newtonian Behavior of Black Liquors:

For all Newtonian liquids the rate of shear is proportional to the shear stress applied if this behavior is not exhibited by the fluid, it is called non-Newtonian. It may behave as a pseudo plastic dilatent, or a Bingham plastic fluid with or without yield value.

The test for the non-Newtonian behavior can be done by varying whether the rate of shear is proportional to the shear stress applied or not. For this, measurements of the rate of shear and stress are necessary, which may be only obtained from Stormer viscometer. Since the shear stress in case of Stormer viscometer is proportional to the weights applied

Equation 3-21 and the rate of shear is proportional to the reciprocal of the time for 100 revolution Equation 3-20 a graph of weights applied versus reciprocal of time should be equivalent to the shear stress applied versus rate of shear.

If the liquid is Newtonian, the curve obtained should be straight line passing through the origin if not it is non-Newtonian.

EXPERIMENTAL PROCEDURE

Capillary Viscometer:

Sample of liquid was charged through tube (1) to the bulb A, Figure 3-1. Viscometer was placed in a constant temperature bath for about 30 minutes. By applying suction liquid was raised to the bulb C and was allowed to fall freely under gravity. Efflux time, the time required for the level to fall from D to E was noted.

In case of modified Cannon Fensky viscometer for opaque liquids, the viscometer was inverted dipping the tube F in the sample and applying suction to the tube G, known amount of sample was charged into the bulb A. Both tubes F and G were closed. Viscometer was kept vertical in the temperature bath for about 30 minutes. Opening the tubes F and G, allowed the liquid to rise. Time for the level to rise from D to E was noted. Experiment was repeated twice to get consistent readings at each temperature. Detailed procedures are available in (14).

Calibration of the capillary viscometer was done with distilled water and standard glycerol solutions and the viscometer constant k_c was calculated.

Stormer Viscometer:

The rotor was positioned in the spindle so that the eccentricity or runout was minimized. The cup was centred with respect to the rotor with the adjustable screws in the supporting platform. Care was taken to see that the cup does not touch the rotor at the bottom side. The position was marked and the sample was placed in the cup to a standard depth. Weights were added to the string, the brake released and the time for 100 revolutions was recorded. The experiment was repeated two to three times to get consistent readings. At higher concentrations above 44% experiment was repeated for 3-4 weights and the values of apparent viscosity at a particular speed (30 rpm used here), was recorded.

Test for Non-Newtonian Behavior of Black Liquors:

A series of experiments were conducted to determine if bamboo and bagasse black liquors exhibit non-Newtonian behavior at higher concentration. Fixed volumes of samples were taken in the cup and the time taken for 100 revolutions of the rotor was determined for 3-4 weights applied. Experiment was done for various concentration starting from 54% to 44% and the values of time for 100 revolution were noted down.

RESULTS AND DISCUSSIONS

Tables 3-1 to 3-4 show the experimental data obtained for bamboo, bamboo + salaiwood, bagasse and eucalyptus samples respectively. Figures 3-1 to 3-4 show the variation of viscosity with respect to concentration at three different temperatures viz at 50°C, 70°C, 90°C for bamboo, bamboo + salai, bagasse and eucalyptus black liquor samples respectively.

It may be observed from Figures 3-1 to 3-4 that at 50°C the slopes of the viscosity concentration curve changes from 1.0 to 3.0 for bamboo, 1.5 to 2.0 for bagasse and 2.0 to 2.5 for eucalyptus black liquors for the concentration change 30 to 45% solids.

Figure 3-1 shows that an increase in temperature from 50 to 70°C decreases the viscosity of bamboo black liquor by 30 percent at 20% solids concentration and by 90% at 50 percent solid concentration. The viscosity of 20% and 50% bamboo black liquor decrease by 25% and 66% of their values at 70°C as the temperature of the liquor increases to 90°C. Similar behavior is observed for the other black liquors samples used in this work.

The viscosities of various black liquors at 70°C are compared in Figure 3-5. Harvin's[3] viscosity data for pine black liquor are also included in the Figure 3-5. This figure shows that bagasse has higher viscosity than all other samples

investigated. At 45 percent concentration viscosity of bagasse is 8 times that of eucalyptus, 10 times that of bamboo, 25 times that of bamboo + salai wood and 100 times that of pine liquor. These ratios are much smaller at lower concentration. At 30% solid concentration bagasse is 5 times more viscous than eucalyptus 7 times bamboo, 15 times pine liquor. The higher viscosity ofbagasse black liquor may be attributed to the higher amounts of pentosans of bagasse (Table 1-1). The alkaline pulping reactions would cause easy degradation and dissolution of these pentosons.

Tables 3-5 and 3-6 show experimental data necessary to evaluate the non-Newtonian behavior of bagasse and bamboo black liquors for the concentration range of 44.55 percent solids. Figures 3-6 and 3-7 show the plot of weights used in stormer viscometer versus the reciprocal of time for 100 revolutions. It may be observed from these figures that the devation from Newtonian behavior occurs between 46-48 percent and 44-45 percent for bamboo and bagasse black liquors respectively at 50°C. The shape of the curves shows that the black liquors behave like Bingham plastic at higher concentration above 45% solids with a yield value of shear stress.

It is natural that this non-Newtonian behavior of black liquors would vary with temperature, the deviation from Newtonian behavior being less as the temperature increases and ultimately tending to become Newtonian.

Figure 3-8 shows the Newtonian behavior of eucalyptus, bamboo, bamboo + salai, black liquors at 40 percent concentration and 19°C. Here instead of plotting weights versus reciprocal of time a graph of time versus reciprocal of weight has been plotted. All the curves are straight lines passing through the origin. Hence it may be concluded that all black liquors exhibit Newtonian behavior below 40 percent solid concentration at a temperature of 19°C and above.

Table 3-7 shows a comparison between eucalyptus black liquor from laboratory and commercial scale pulpings, at 12.5% concentration. It shows that the viscosity for eucalyptus black liquor from commercial scale pulping is 3 percent higher than the values of black liquor from laboratory scale pulping. Hence the values of viscosity of laboratory eucalyptus sample can be conveniently used for process engineering calculations.

The viscosity results for bagasse black liquors obtained in this work are compared with data available in literature.[15] The values compare well at lower concentration upto 25 percent solids.

The deviations at higher concentrations (25-53% solids) are as large as 4-90% based on the bagasse liquor ofthis investigation. The differences may be attributed to pulping processes used, kraft black liquor was used in this work whereas soda black liquor was used by Lal.[15]

Values of viscosity in the Figures 3-1 to 3-4 can be used for process engineering calculations. Viscosity values for 100°C temperature and above, at which the most of the operation after multiple effect evaporators are conducted, can be obtained by extrapolating the graph of viscosity versus temperature and can successfully be used in all the calculation.

TABLE 3-1: VISCOSITY OF BAMBOO BLACK LIQUOR

% Solids	Temp., °C	Viscosity C.P.	% Solids	Temp., °C	Viscosity C.P.
13.5	24.8	2.10	38.00	51.3	31.4
	41.0	1.87		59.5	21.5
	51.22	1.52		69.5	15.1
	60.2	1.45		80.5	11.45
	69.5	1.11		87.00	10.82
	79.65	.95		96.00	8.70
	90.9	.81	44.5	51.15	408.00
26.00	30.4	7.00		59.6	216.5
	40.4	5.00		69.5	134.5
	45.5	4.43		80.5	56.2
	50.2	3.86		87.00	42.80
	60.2	3.13		96.00	29.05
	65.7	2.76	61.1	65.00	12700
	69.5	2.58		69.00	6450
	75.1	2.40		75.00	4350
	79.7	2.24		86.00	1740
	90.00	1.98			
	96.00	1.84			

TABLE 3-2 VISCOSITY OF BAMBOO + SALAI WOOD BLACK LIQUOR

% Solid	Temp., °C	Viscosity C.P.	% Solid	Temp, °C	Viscosity c.p.
14.3	24.8	2.45	34.5	69.50	5.41
	41.00	1.68		79.60	4.27
	51.20	1.34		90.90	3.46
	60.40	1.11	44.3	26.10	120.20
	69.00	1.04		50.00	62.20
	79.60	0.83		55.60	53.70
	90.90	0.72		63.00	44.30
24.5	24.80	5.77		74.80	28.08
	41.00	3.72		81.30	27.45
	51.20	2.86	58.1	48.50	9310
	60.40	2.40		60.00	2050
	69.50	2.02		78.00	462
	79.60	1.69		88.00	270
	90.90	1.43	60.2	85.00	549
34.5	24.80	14.70		75.00	1105
	41.00	11.62		64.00	3125
	51.20	8.23		55.00	10120
	60.75	6.76			

TABLE 3-3: VISCOSITY OF EUCALYPTUS (LABORATORY PULPING) BLACK LIQUOR

% Solids	Temp., °C	Viscosity c.p.	%Solids	Temp., °C	Viscosity c.p.
19.42	35.0	1.95	28.0	80.7	4.08
	40.0	1.70	42.0	25.4	466.00
	50.0	1.39		40.2	173.20
	60.0	1.22		49.2	111.30
	65.0	1.17		59.6	60.00
	70.0	1.02		60.6	43.80
	79.5	0.81		79.8	32.25
28.00	25.0	22.50		90.4	25.65
	34.8	16.09	56.00	83.0	69.20
	40.5	11.45		70.0	3020
	49.9	8.77		63.00	9790
	60.1	7.03		53.00	42200
	69.4	6.13			

TABLE 3-4: VISCOSITY OF BAGASSE BLACK LIQUOR

% Solids	Temp., °C	Viscosity c.p.	%Solids	Temp., °C	Viscosity c.p.
14.5	29.10	9.50	33.5	73.00	50.00
	54.00	4.78		85.00	39.40
	73.20	3.12	44.3	49.00	2705
	85.50	2.45		50.40	2695
27.5	91.10	10.30		66.20	1110
	78.10	14.30		79.00	598
	65.10	21.90		93.00	444
	53.20	31.40	50.00	49.00	12900
	32.00	65.30		67.00	3280
33.5	35.00	188.30		79.50	1620
	46.80	108.8		91.50	982
	61.20	69.20			

TABLE 3-5: DATA FOR EVALUATING NON-NEWTONIAN BEHAVIOR OF BAGASSE BLACK LIQUOR AT 50°C

% Solids	Weight added gm.	Time for 100 revolutions T min.-sec.	1/T, Sec^{-1}
50.0	1000	11-55	0.00140
	1200	7-408	0.00217
	500	33-20	0.000502
48.0	1000	4-38	0.0036
	800	5-57	0.0078
	600	8-47	0.0019
	400	18-30	0.0009
46.0	1000	2-9	0.00775
	800	2-41	0.0062
	600	3-33	0.0047
	400	5-45	0.0029
	200	16-40	0.001
45.0	800	2-5	0.008
	600	2-47	0.006
	400	4-10	0.004
	100	20-50	0.0008
44.5	400	3-20	0.0050
	200	6-40	0.0025
	50	27-50	0.0060

TABLE 3-6: DATA FOR EVALUATING NON-NEWTONIAN BEHAVIOR OF THE BAMBOO BLACK LIQUOR AT 50°C

%Solids	Weight added gm.	Time for 100 revolution T, Min -Sec.	1/T, Sec^{-1}
54.0	1500	8-00	0.00208
	1000	11-54	0.00140
	500	40-40	0.00041
	1200	9-15	0.00174
52.0	1000	4-36	0.00360
	500	10-10	0.00164
	300	40-00	0.004
50.0	1000	1-57.8	0.0085
	300	6-32.6	0.00254
	600	3-24	0.0049
48.0	500	1-44.6	0.00957
	400	2-12	0.0076
	300	2-58.8	0.0056
	100	12-50	0.0013
46.00	300	1-22	0.0122
	150	2-53	0.006
	50	8-20	0.002
45.0	50	5-12	0.0032
	100	2-46	0.0065
	200	1-17	0.013

TABLE 3-7: VISCOSITY OF EUCALYPTUS BLACK LIQUOR

Temperature	Viscosity, cp Commercial Sample*	Viscosity, cp Laboratory sample**	% Diff.
33.5	1.570	1.280	1.97
48.8	1.140	0.918	2.20
61.0	0.937	0.720	3.00
74.2	0.770	0.590	3.05

*12.5 percent solids black liquor

**extrapolated values for 12.5 percent solids black liquor

TABLE 3-8: COMPARISON OF VISCOSITIES OF BAGASSE BLACK LIQUORS

% Solids	Temperature, 50°C			Temperature, 100°C		
	Viscosity* c.s.	Viscosity** c.s.	% Diff.	Viscosity* c.s.	Viscosity** c.s.	% Diff.
15.50	4.90	5-47	-10.42	2.150	2.075	+3.62
24.70	14.45	18.10	-20.10	5.25	3.38	+55.3
35.4	75.50	133.8	-43.7	16.5	29.20	-43.5
45.6	247.00	2430.0	-90	49.0	220.00	-77.8
				171	1210	-85.8

*as published in (15)

**Bagasse black-liquor of this investigation

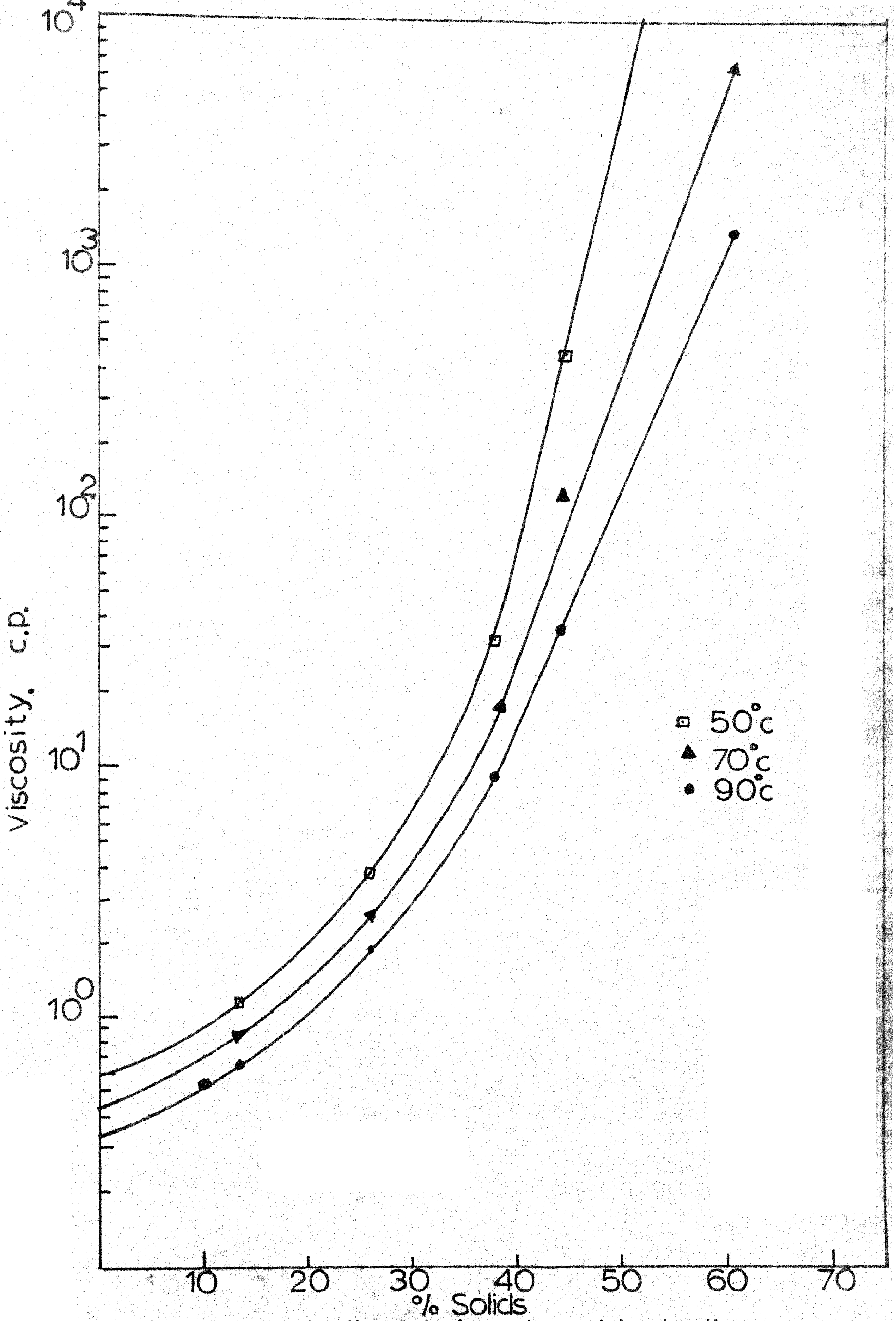


Fig. 3-1 Viscosity of bamboo black liquor

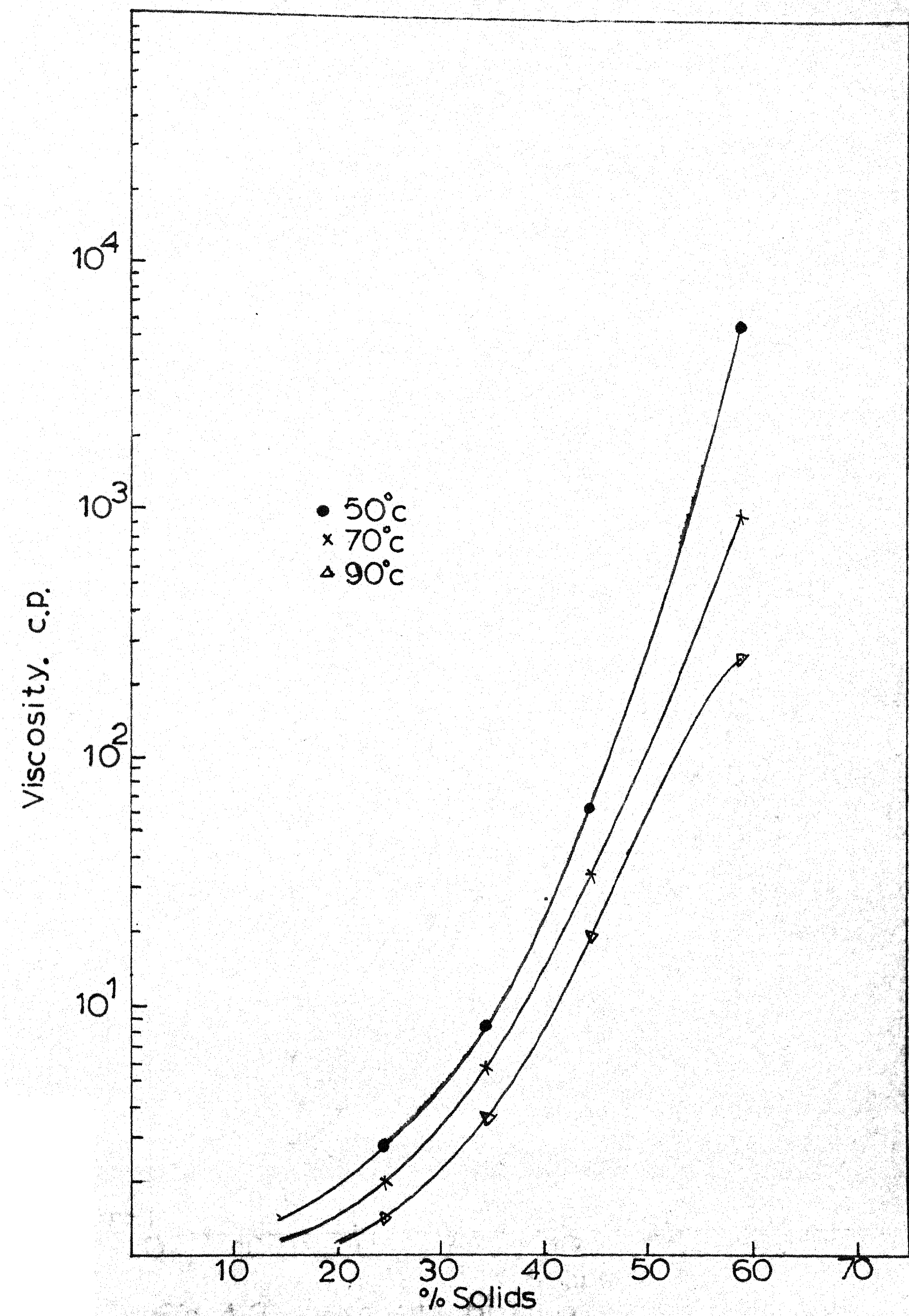


Fig.3-2 Viscosity of bamboo+ salai(10%) black liquor

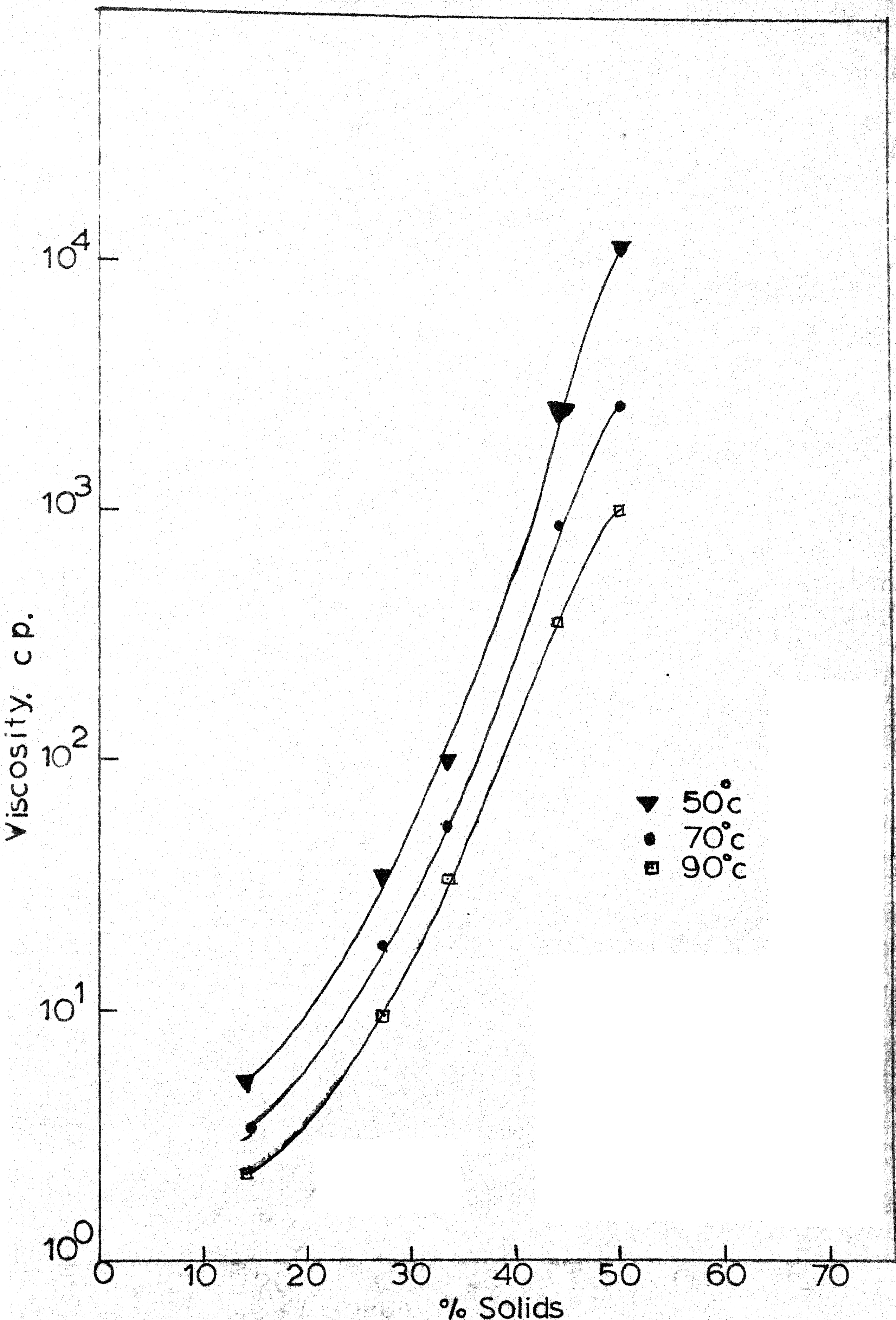


Fig. 3-3 Viscosity of bagasse black liquor

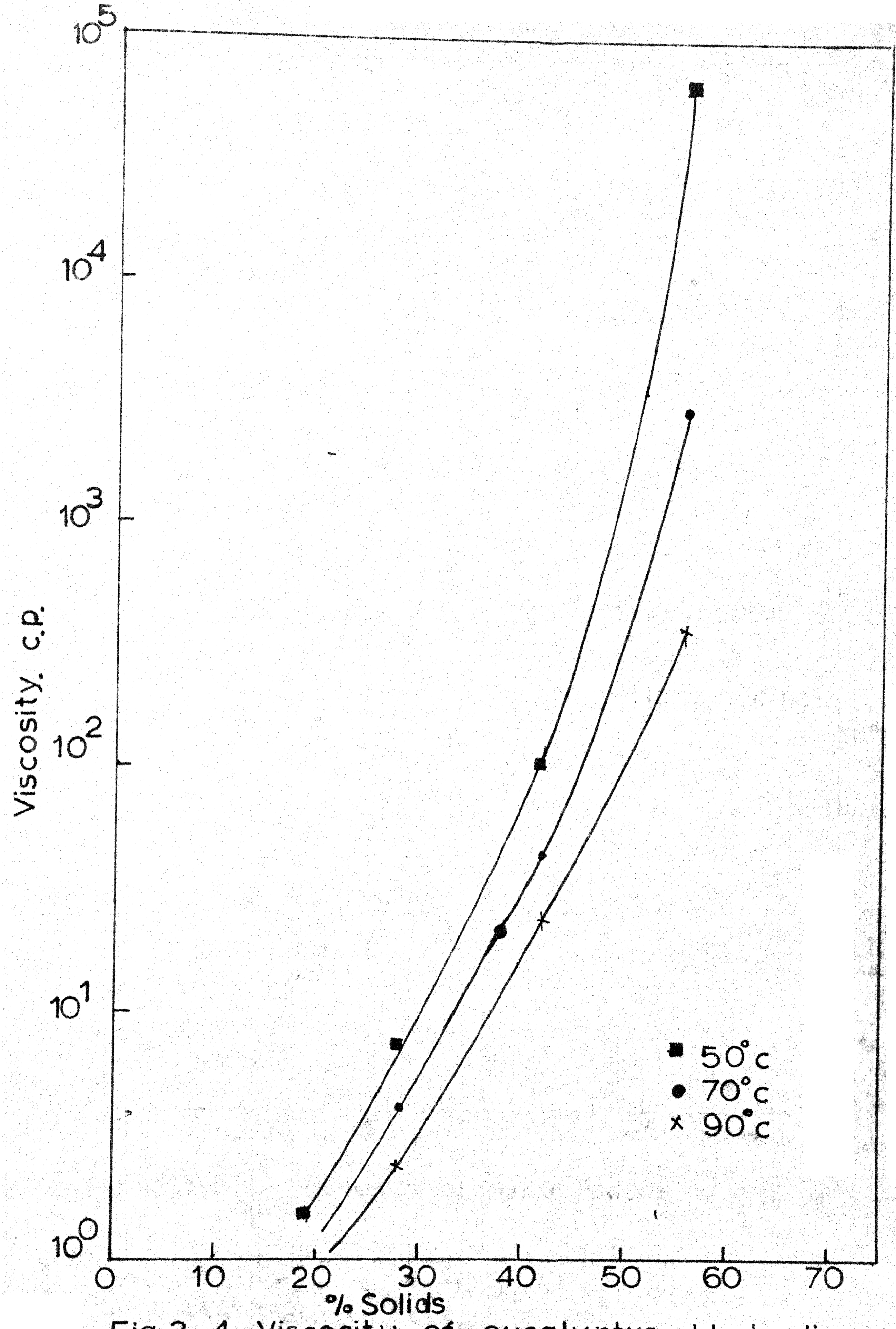


Fig. 3-4 Viscosity of eucalyptus black liquor

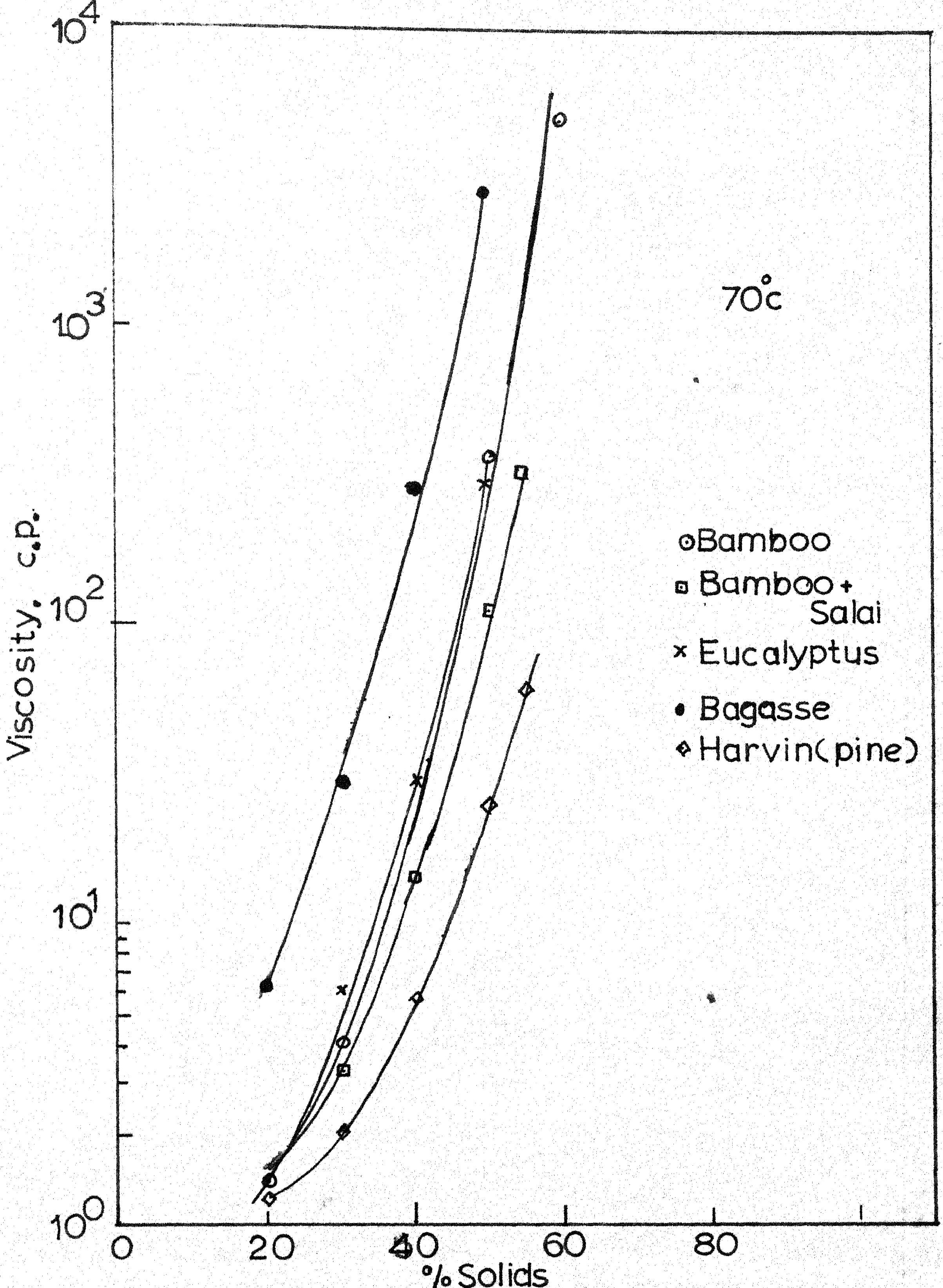


Fig. 3-5 Viscosity of black liquors

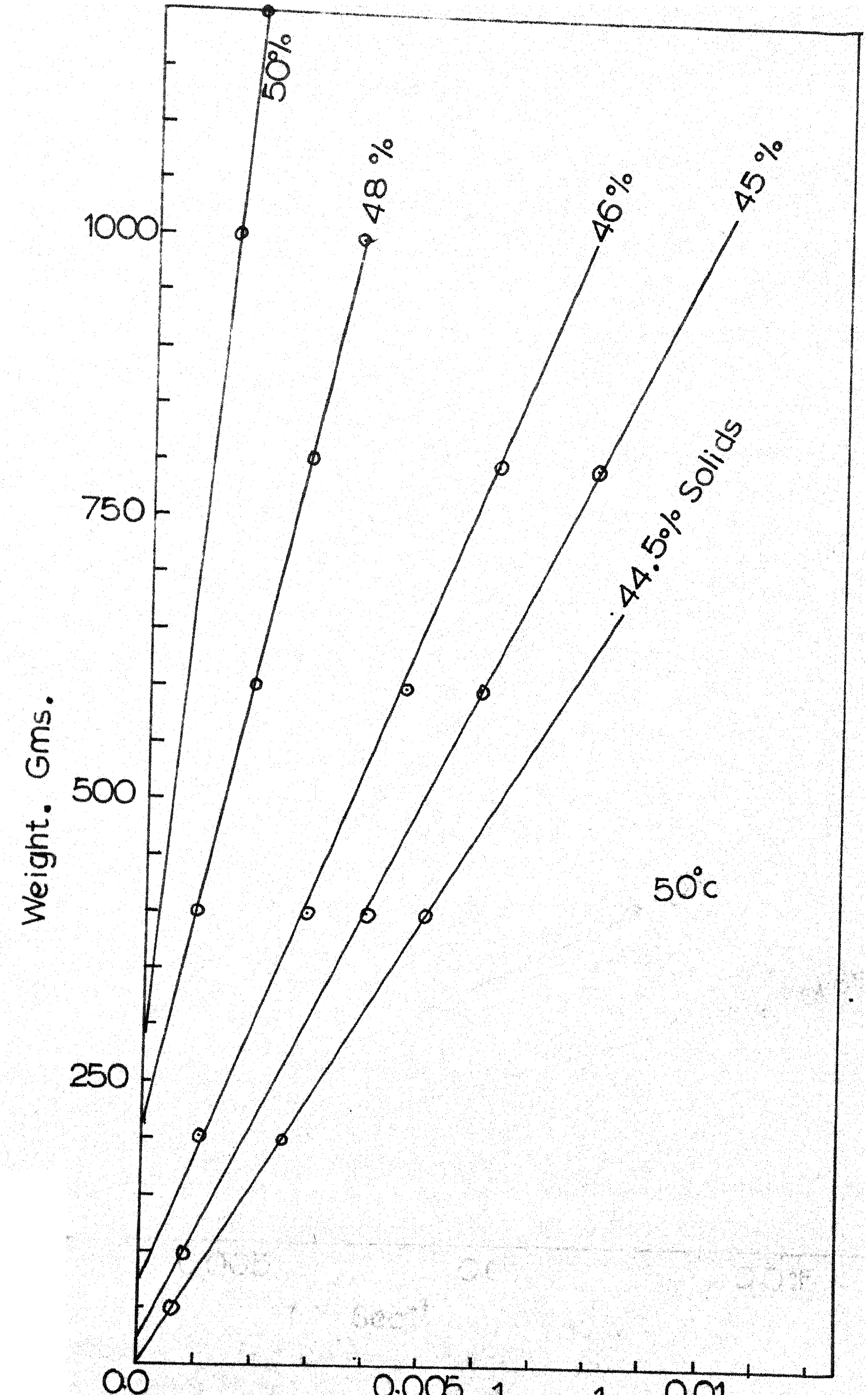


Fig. 3-6 Test for non-Newtonian behavior of bagasse black liquor using Stormer viscometer

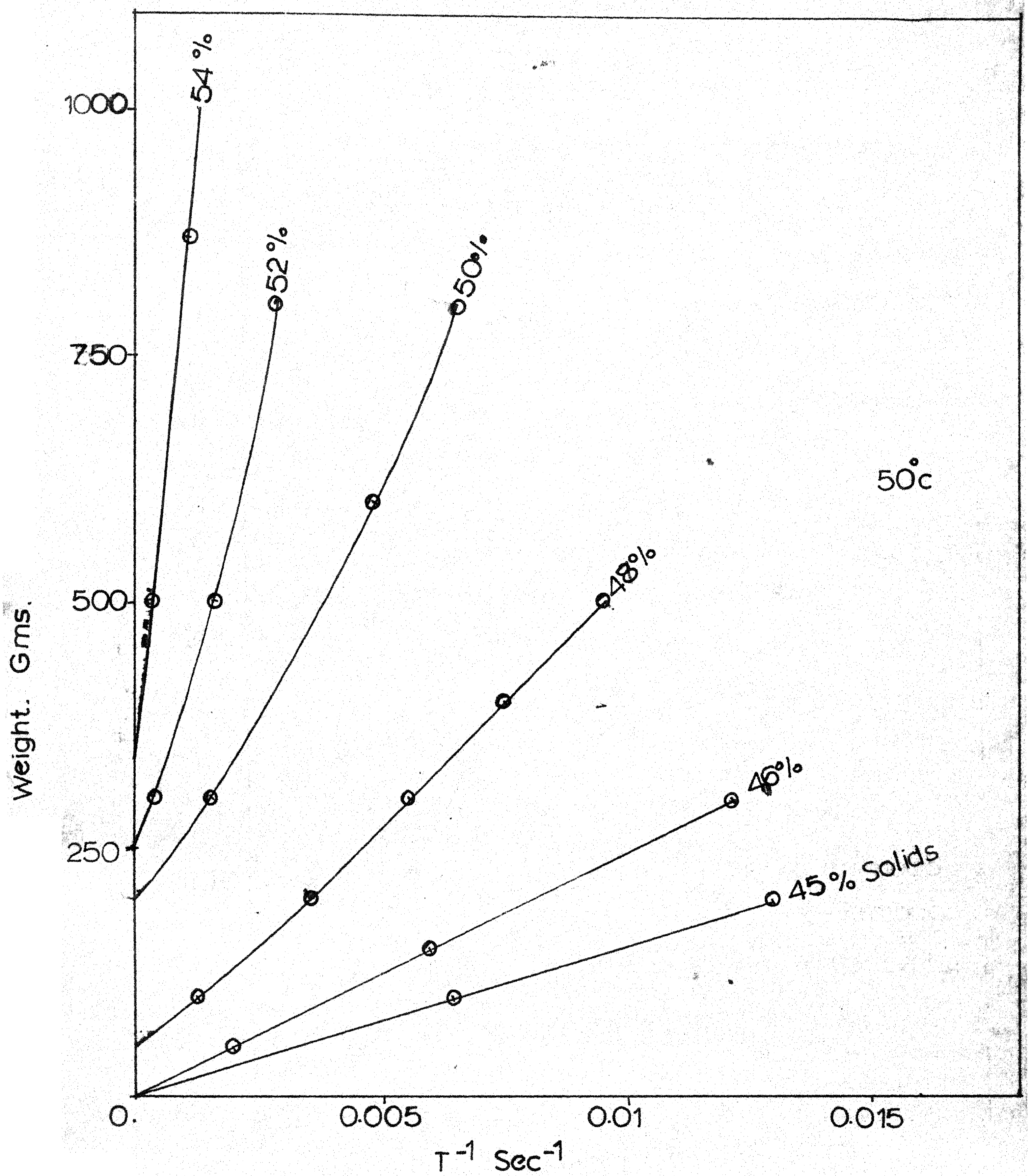


Fig. 3-7 Test for non Newtonian behavior of bamboo black liquor using Stormer viscometer

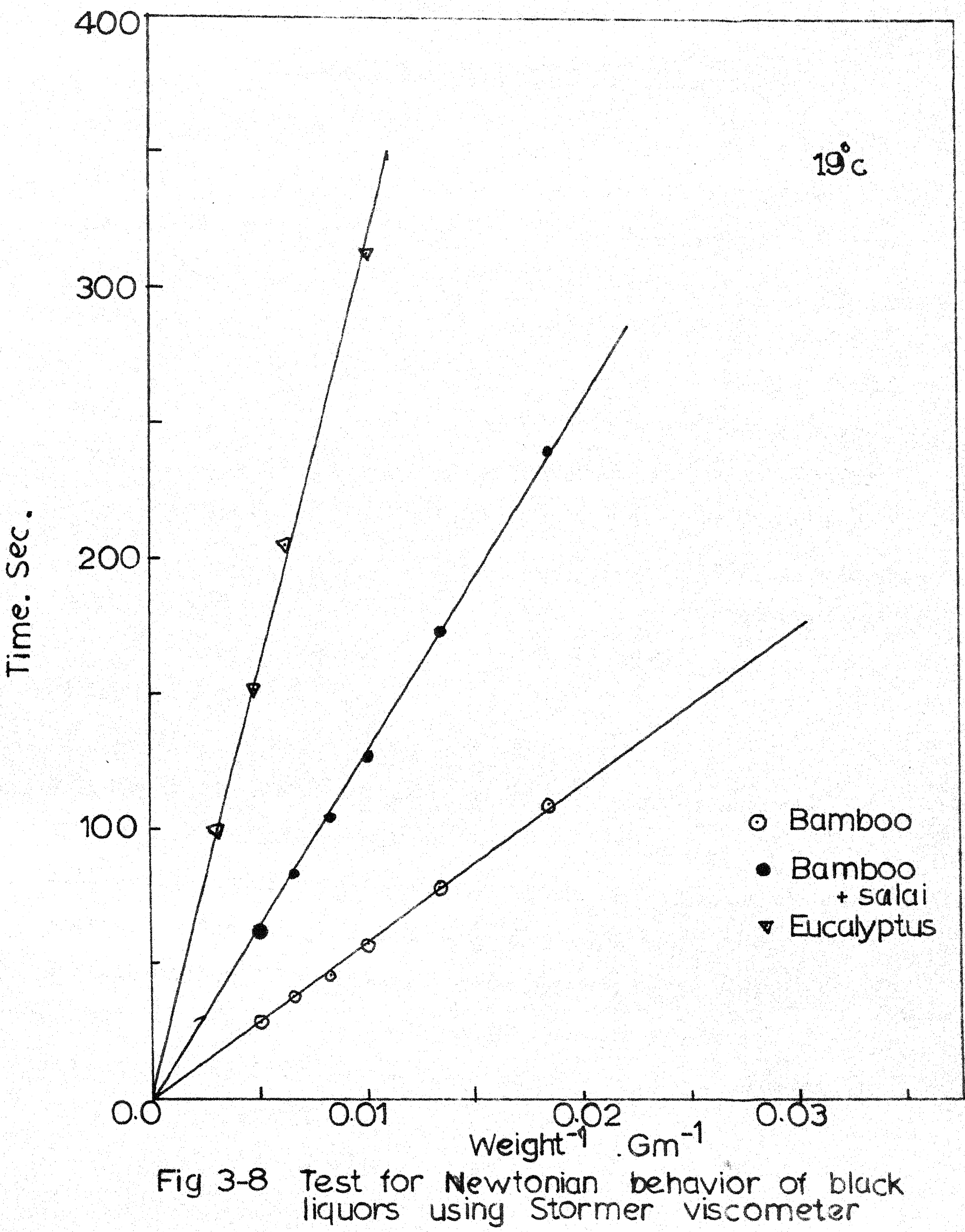


Fig 3-8 Test for Newtonian behavior of black liquors using Stormer viscometer

CHAPTER IV

THERMAL CONDUCTIVITY OF BLACK LIQUORS

The weak black liquor (12-20% solids) from the pulping and washing operations is concentrated in multiple effect evaporators (usually 4-7 effects). Steam consumption and evaporation rates of these multiple effect evaporators are determined by the overall heat transfer coefficient controlled by the characteristics of the liquor processed. Values of the thermal conductivity of black liquors are necessary to calculate Nusselt and Prandtl numbers used in convection heat transfer correlations. Tsederberg[19] has outlined the procedure for predicting thermal conductivities of simple solution of electrolytes and nonelectrolytes. This work deals with the experimental determination of thermal conductivity of bamboo and bagasse black liquors.

Thermal conductivity is a measure of amount of heat flowing per unit cross-section through unit thickness of material in unit time per unit temperature gradient. There are three different cell designs available for the experimental determination of thermal conductivity of liquids. The earliest method of Schleiermacher[20] utilizes a fine platinum wire embedded in a closed cylinder as the constant temperature heat sink. The method suffers from the disadvantages of correct orientation of the wire along the central axis of the cylinder, heat losses from the ends of the wire and natural convection effects. The

second method minimizes natural convection currents by filling the space between two horizontal plates with the liquor and supplying heat from the upper plate. Sakiadis and Coates[21] have shown that it is possible to estimate convection current with this arrangement for liquid layer thickness upto about 2.0 inches. An alternate method consists of a system of concentric cylinders with the inner and outer cylinders serving as the heat source and the sink respectively. Though the edge effects are less than the parallel plate design, coaxial orientation of the cylinders and convection currents still pose a problem.

Venart and Krishnamurthy[22] have reviewed thermal conductivity values of several organic liquids. Most organic and nonmetallic liquids have thermal conductivity values in the range of 0.05 to 0.15 Btu/hr.sq.ft.°F/ft. with the exception of ammonia and water ($k = 0.3$ to 0.4 Btu/hr.sq.ft.°F/ft). Generally thermal conductivity of aqueous solutions decrease with an increase in solute concentration, however, solutions of sodium salts possess an opposite effect.[3] The temperature coefficient of thermal conductivity for most of the liquids is positive with a few exception like toluene, nitrobenzene, petroleum fractions, etc.

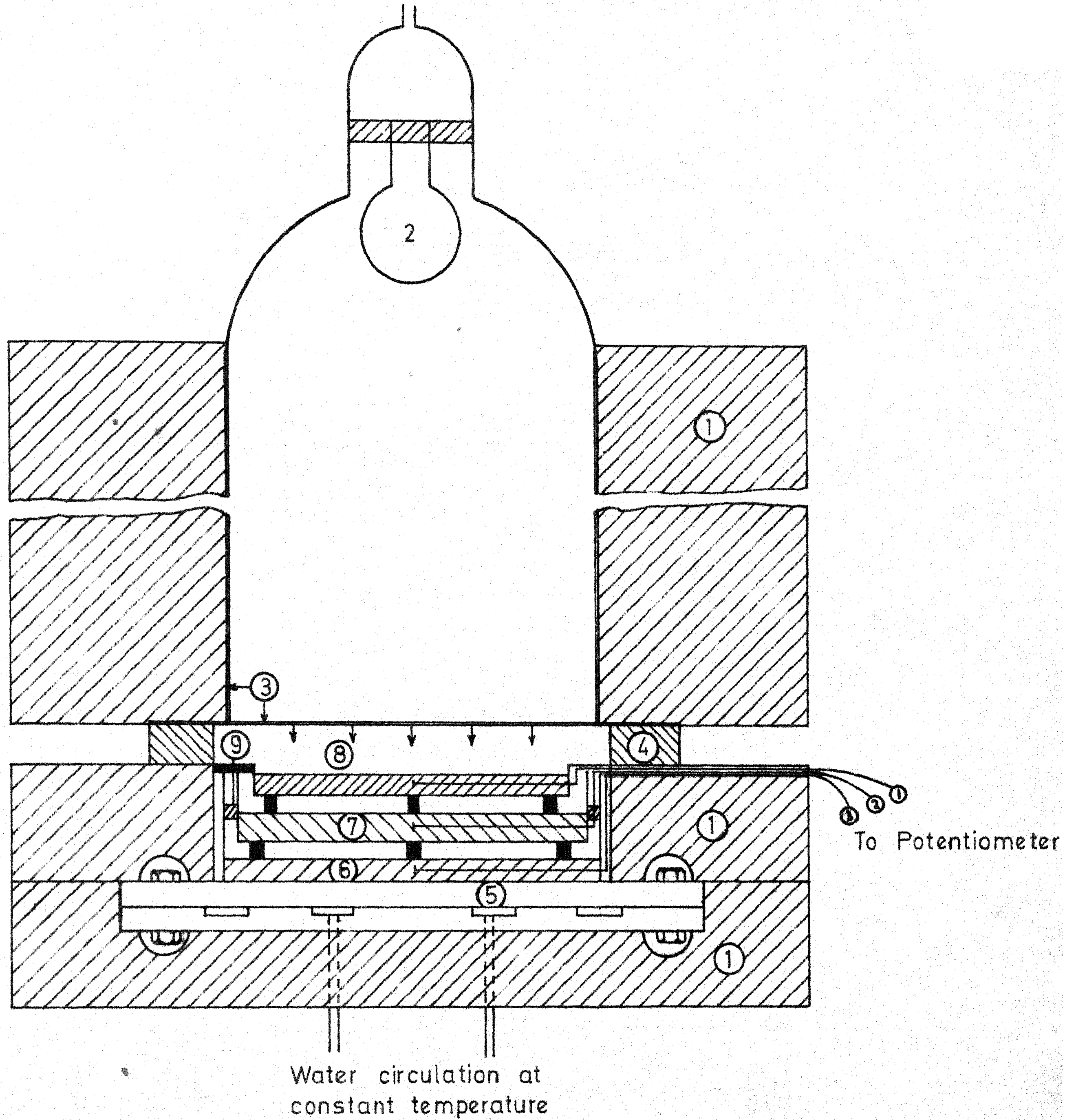
Approximately two thirds of kraft liquor solids usually consists of organic matter and the rest is mainly inorganic compounds. The inorganic compounds are present in the liquor

as their sodium salts. The sodium ions in the black liquor would tend to increase the thermal conductivity values while the organic compounds may tend to decrease its value. Harvin[3] has studied the variation of thermal conductivity of pine kraft black liquor with temperature and concentration using the parallel plate method. The measurement of actual heat flow was avoided in Harvin experiment by using an additional liquid layer of known thermal conductivity and separated from the unknown liquid sample by a metal plate of known thermal conductivity. The temperature distribution across the liquid and metal layers can be used to determine the thermal conductivity of the unknown liquid.

The apparatus used in this work is similar in construction to Harvin's design[3] with minor modifications. Other designs discussed earlier are likely to be less suitable for handling viscous black liquor especially at higher concentrations.

Apparatus:

A schematic sketch of the apparatus is shown in Figure 4-1. It consists of two shallow troughs and a disc of brass placed over a brass plate. This bottom plate rests over another plate and is maintained at constant temperature by circulating water from a constant temperature bath through helical grooves provided. The brass plates and the troughs are nickel plated in order to eliminate any corrosive action of alkaline black liquor. Detailed



1. Insolation (Wood)
2. Infrared Bulb.
3. Polished Stainless Steel Sheet.
4. Rubber Ring Insulation.
5. Constant Temp. Plate Device.
6. Bottom Trough.
7. Middle Trough.
8. Top Plate.
9. Plastic Spacers.

FIG 4-1. Thermal Conductivity Assembly.

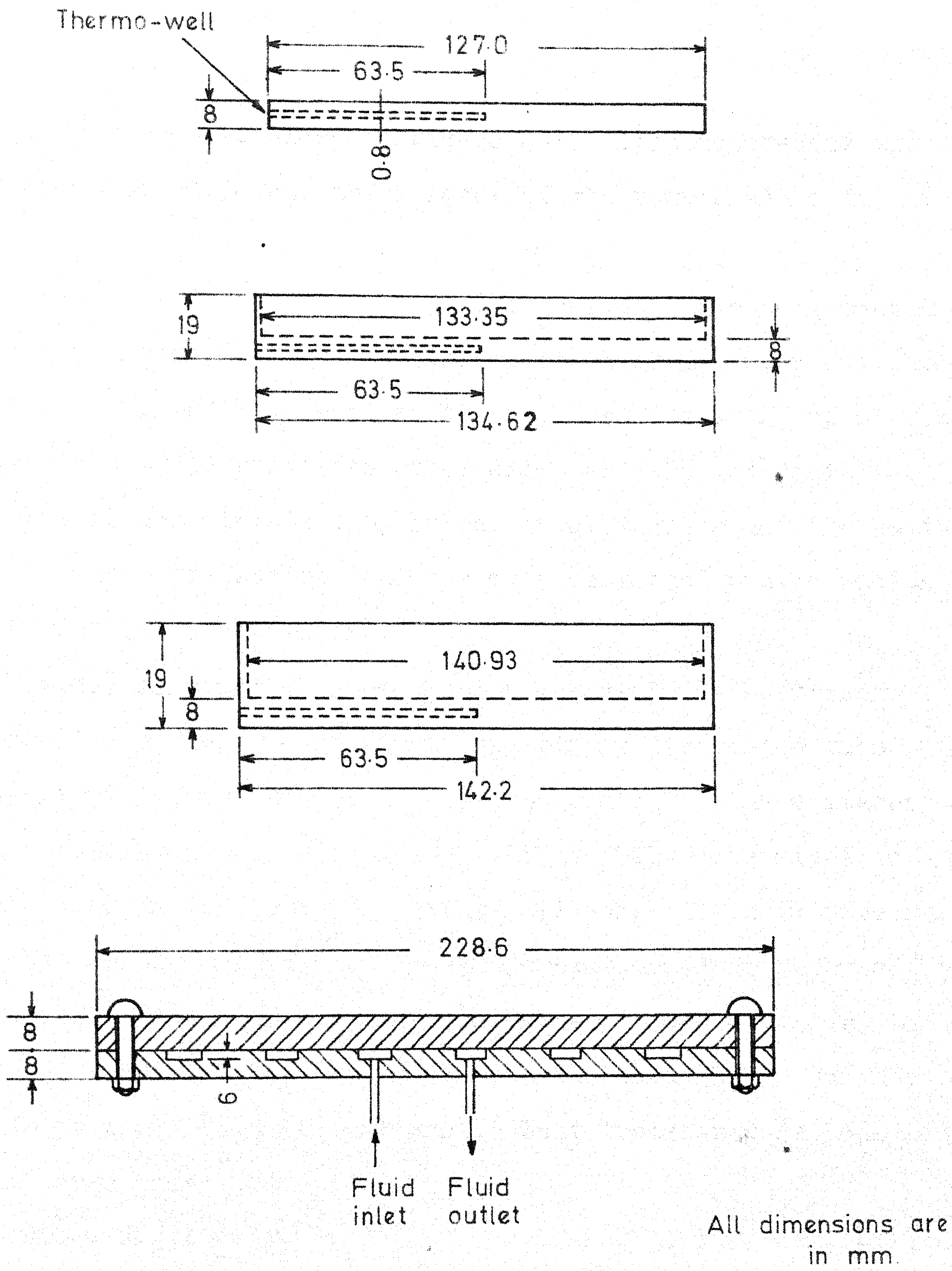


Fig. 4·2. Details of Thermal Conductivity Cell.

cell arrangement is shown in Figure 4-2. Plastic spacers are used to obtain 0.32 cm. thick layer of the sample and standard liquid.

Radiation from an infra red bulb serving as a heat source falls on a finely polished stainless steel sheet (0.08 cm. thick) which in turn radiates heat to the top most disc. A gap of 1.25 cm. exists between stainless steel sheet and the top most disc. Heat losses are minimized by rubber insulation around the bottom most trough. The entire cell assembly is placed inside wooden insulation (12.5 cm. thick).

Copper constantan thermocouples inserted in the troughs and disc to a length of 6.35 cm. and plugged by teflon tube serves to determine the temperature by measuring the voltages with a potentiometer of accuracy 0.05 mV. The determination of the thermal conductivity of black liquors with this apparatus is based on the concept of conduction heat transfer with resistances in series plate-1, liquid layer and upper trough - 21 form an integral part, and the upper trough - 22 liquid layer and the bottom trough-3 form another part. Heat transfer equations for these parts are:

$$Q_{12} = U_{12}\, A_{12}\, \Delta T_{12} \qquad (4\text{-}1)$$

$$Q_{23} = U_{23}\, A_{23}\, \Delta T_{23} \qquad (4\text{-}2)$$

$$\frac{\Delta T_{12}}{Q_{12}} = \frac{1}{U_{12}\, A_{12}} = \frac{0.5\, x_1}{k_1\, A_1} + \frac{x_U}{k_U\, A_{12}} + \frac{x_2}{k_2\, A_{21}} \qquad (4\text{-}3)$$

$$\frac{\Delta T_{23}}{Q_{23}} = \frac{1}{U_{23}\ A_{23}} = \frac{0.5\ x_2}{k_2\ A_{22}} + \frac{x_1}{k_1 A_{23}} + \frac{x_3}{k_3\ A_3} \qquad (4\text{-}4)$$

At steady state operation all the heat transferred to the top most plate should pass to the bottom most plate giving

$$Q_{12} = Q_{23} \qquad (4\text{-}5)$$

Dividing (4-1) by (4-2) we have

$$\frac{\Delta T_{12}}{\Delta T_{23}} = \frac{\dfrac{0.5\ x_1}{k_1\ A_1} + \dfrac{x_U}{k_U\ A_{12}} + \dfrac{0.5\ x_2}{k_2\ A_{21}}}{\dfrac{0.5\ x_2}{k_2\ A_{22}} + \dfrac{x_1}{k_1\ A_{23}} + \dfrac{0.5\ x_3}{k_3\ A_3}} \qquad (4\text{-}6)$$

Knowing all the terms thermal conductivity of the sample can be calculated. Details of sample calculations are given in the Appendix B. .

Experimental Procedure:

Black liquor sample may be taken in either of the troughs. In this work black liquor sample was taken in the upper trough and distilled water in the lower trough.

Measured quantity of black liquor samples was taken in the upper trough and distilled water in the lower trough. The cell was assembled as shown in Figure 4-1 using plastic spacers. Air pockets between the liquid layer and the plate can be removed by slightly tilting the cell assembly. Circumferential gaps maintained by 0.32 cm. plastic spacers were closed by rubber rings to reduce evaporation loss from the liquids.

The disc and the trough assembly was placed over the constant temperature plate and the insulation wood is placed in position. Infrared bulb was switched on and water circulation was simultaneously started. Temperature in the bath was maintained slightly below the temperature at which the thermal conductivity of liquid was to be determined.

When steady state was reached usually after 1.5 to two hours as determined by constant temperature readings, emf readings were taken by potentiometer.

The apparatus was tested with distilled water and toluene, and the variation in thermal conductivity values was within $\pm$ 3% ofthe values reported in literature.[3]

Precautions:

The following precautions are necessary to obtain consistent and reliable results.

1. Perfect metal to metal contact is necessary between the bottom most trough and the constant temperature plate. This was taken care of during fabrication of the apparatus itself.

2. Major error may be caused by the heat losses from the apparatus. This can be minimized by proper insulation to get consistent results.

3. Accurate measurements of the temperature are necessary to obtain reliable data of thermal conductivity.

4. The errors causes by air bubbles forming in water and black liquors was eliminated by boiling water just before use and

by keeping black liquor under vacuum of 4 cm. Hg for about 30 minutes.

Results and Discussions:

Experimental results are presented in Tables 4-1 and 4-2 for bagasse and bamboo black liquors respectively. The values of emf ratios reported assumes a linear relationship of emf and temperature.

The calculated values of the thermal conductivity of bagasse and bamboo black liquors are given in Tables 4-1 and 4-2 respectively. The data are graphically correlated in Figure's 4-3 and 4-4 for bagasse and bamboo black liquors respectively. A comparison of thermal conductivity values of bamboo and bagasse and pine black liquors[3] at 70°C is shown in Figure 4-5. The thermal conductivity values of black liquors are 4 percent higher than bamboo black liquors at 50 percent solid concentration and 70°C.

The higher thermal conductivity values of bagasse may be caused by the larger portion of inorganics to bagasse black liquors. The ratio of organic to inorganic chemicals is 1.0 cms. and 1.54 for bagasse and bamboo black liquors respectively. The higher proportion sodium salts in bagasse black liquor tend to increase its thermal conductivity.

A comparison of thermal conductivity values at 70°C in Fig.4-5 shows that the pine and bamboo black liquors thermal conductivity values agree closely.

Equations 4-7 and 4-8 represent experimental data obtained for bagasse and bamboo black liquors with an error less than 2 percent.

$$k = 0.50576219 - .256821 \times 10^{-2}\,c + (.89928 \times 10^{-3} + .749 \times 10^{-5}c)T \qquad (4\text{-}7)$$

$$k = (0.53354269 - .3425 \times 10^{-2}c) + (.11355 \times 10^{-2} + 0.209 \times 10^{-5}c)T \qquad (4\text{-}8)$$

where c is in percent solids, T in °C and is kcal/hr sq.m.°K/m.

Equations 4-9 and 4-10 using six constants fit the experimental data with an error less than 0.6 percent.

$$k = (0.42715 - .2377 \times 10^{-2}c) + (.3525 \times 10^{-2} - .284 \times 10^{-6}c)T - (0.2093 \times 10^{-4} - .11 \times 10^{-6}c)T^2 \qquad (4\text{-}9)$$

$$k = (0.59725 - 0.597 \times 10^{-2}c) - (.908 \times 10^{-3} - 0.832 \times 10^{-4}c)T + (.1561 \times 10^{-4} - .61 \times 10^{-6}c)T^2 \qquad (4\text{-}10)$$

where k is in Kcal/hr.sq.m.°C/m.

The compilation of thermal conductivity values for bagasse and bamboo black liquors for different concentration and temperature levels is given in Tables 4-3 and 4-4, based on the use of Equation 4-7 and 4-8 respectively. Correlating equations 4-7 and 4-8 would be convenient for use with computer programming ofprocess engineering calculation.

TABLE 4-1: THERMAL CONDUCTIVITY DATA FOR BAGASSE BLACK LIQUOR

% Solids	Temperature of Water °C	Temperature of Black liquor °C	emf ratio water/black liquor	Thermal Conductivity Water Kcal/hr.sq.m.°K/m.	Thermal Conductivity Black Liq. Kcal/hr.sq.m.°K/m.
15.5	44.6	47.54	0.834	0.547	0.5119
	60.87	62.90	0.848	0.564	0.5328
	79.08	81.02	0.840	0.576	0.5482
33.5	45.45	47.80	0.740	0.550	0.4732
	62.30	64.51	0.790	0.564	0.4939
	81.17	84.14	0.792	0.563	0.5165
50.00	47.09	50.18	0.710	0.550	0.4390
	68.24	71.28	0.733	0.570	0.4700
	85.44	89.28	0.750	0.578	0.4881

TABLE 4-4: THERMAL CONDUCTIVITY OF BAMBOO BLACK LIQUOR

Temp.,°C	Percent Solids				
	20	30	40	50	60
30	0.478	0.450	0.424	0.398	0.372
50	0.505	0.480	0.457	0.432	0.408
70	0.524	0.500	0.476	0.450	0.426
90	0.538	0.518	0.496	0.476	0.454

TABLE 4-3: THERMAL CONDUCTIVITY OF BAGASSE BLACK LIQUOR

Temp.,°C	Percent Solids				
	20	30	40	50	60
30	0.484	0.462	0.440	0.414	0.394
50	0.510	0.488	0.466	0.443	0.420
70	0.530	0.510	0.490	0.470	0.448
90	0.543	0.530	0.513	0.496	0.480

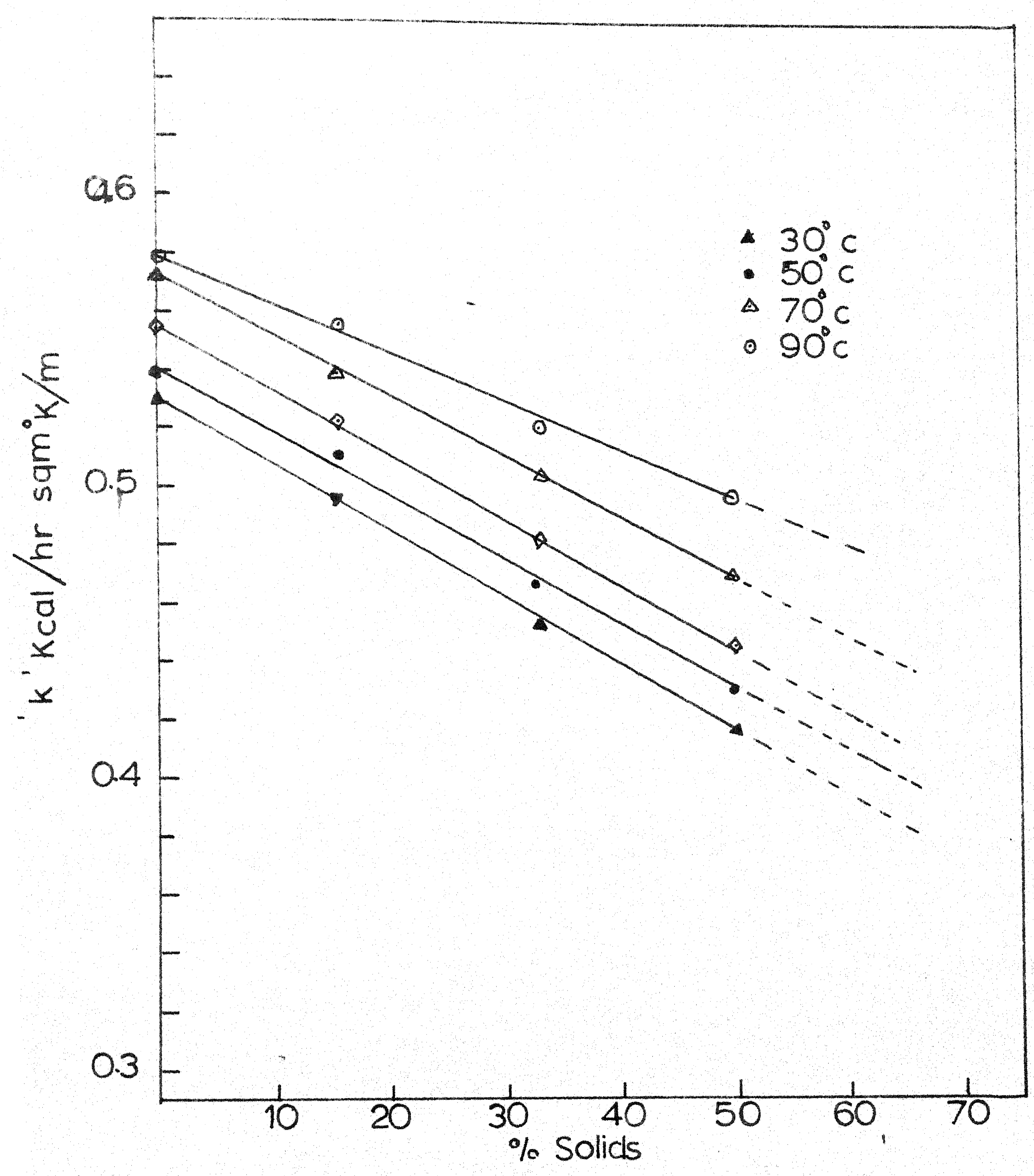


Fig 4-3 Thermal conductivity of bagasse black liquor.

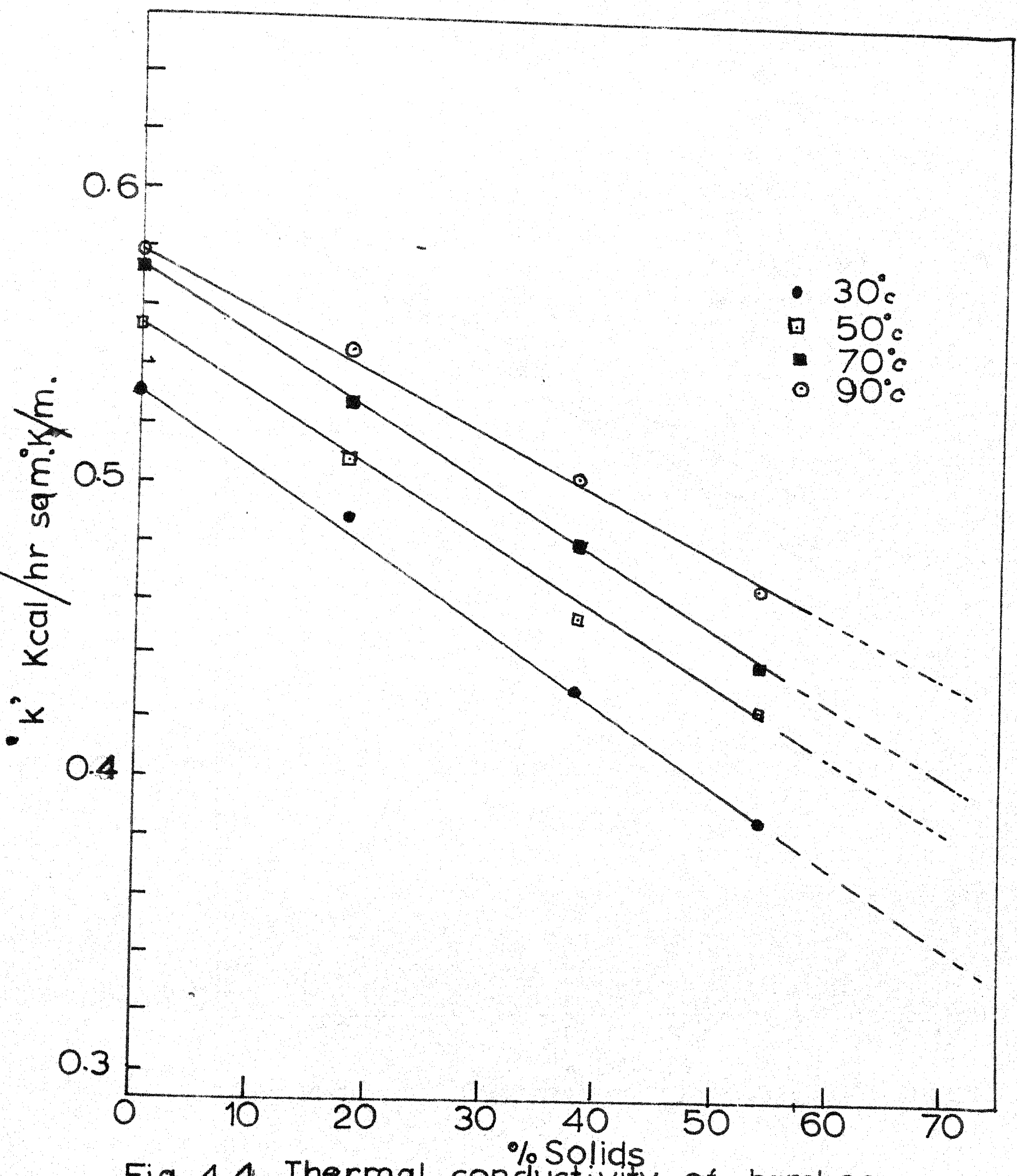


Fig 4-4 Thermal conductivity of bamboo black liquor.

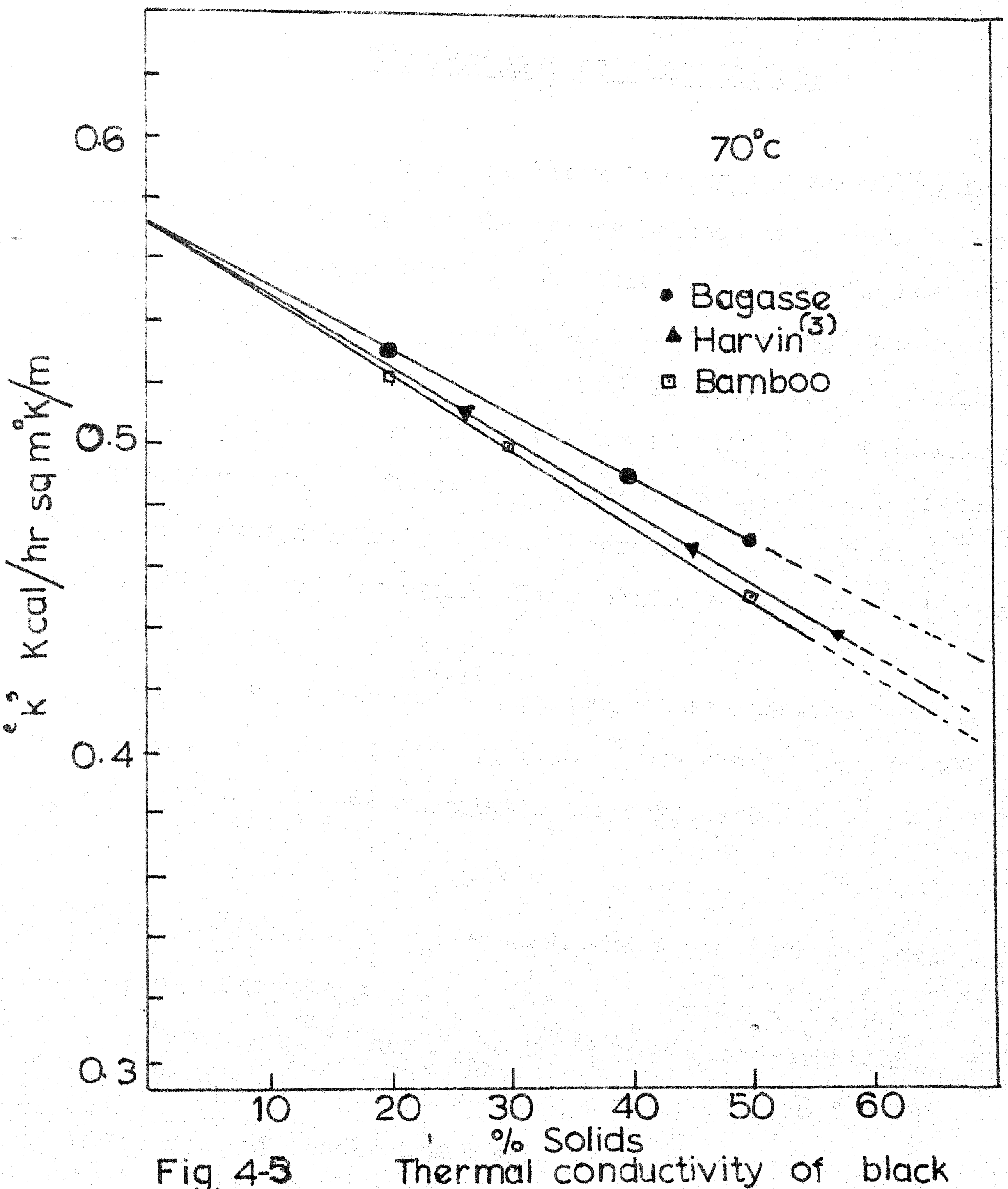


Fig. 4-5 Thermal conductivity of black liquors.

CHAPTER V

SPECIFIC HEAT OF BLACK LIQUORS

Specific heat data for black liquors are necessary for computing the enthalpy and the energy balance calculations for the chemical recovery units in the pulp mill. Specific heat of black liquors would vary with changes in temperature and compositions and concentration of the black liquor. The complexity of the black liquor constituents makes it difficult to estimate the specific heat by theoretical models. Such data are often determined experimentally Kobe and Sorenson[16], Stevenson[17] and Harvin[3] have determined the specific heat of black liquors for North American wood species.

Kobe and Sorenson[16] determined the specific heat of sulphate black liquors from pulping of western hemlock in the range of 25 - 94°C and correlated the data by Equation 5-1.

$$C_p = 0.98 - 0.52\ c \tag{5-1}$$

Equation 5-1 gives the mean specific heat and does not include the effect of temperature.

Stevenson[17] has given Equation 5-2 for predicting the specific heat of black liquor using a value of 0.28 for the specific heat of black liquor solids.

$$C_p = 1.00 - (1.0 - C_{p\ BLS})c \tag{5-2}$$

The prediction from Equation 5-2 would be approximate

since it ignores the effect of temperature on the specific heat of black liquor solids.

Harvin's[3] data represented by Equation 5-3 represents specific heat as a function of temperature and concentration. His results showed that specific heat of pine black liquor solids was 0.42 - 0.50 cal/gm.°C

$$C_p = 0.990 + 8.0 \times 10^{-5}\ T - (0.639 - 6.4 \times 10^{-4} T)c \qquad (5\text{-}3)$$

where T is in °F and c is percent solids.

Specific heat of bagasse black liquor was studied in this work by the usual calorimetric method[18] which is simple, and gives reliable values of specific heat for engineering calculations.

Equation 5-4 represents the energy balance for the calorimeter containing a known quantity of the liquid.

$$Q = (W.C_p + C.E.)\ \bar{T} + Q_L \qquad (5\text{-}4)$$

$$\frac{dQ}{d\theta} = (W.C_p + C.E.)\frac{dT}{d\theta} + \frac{dQ_L}{d\theta} \qquad (5\text{-}5)$$

If at any time θ supply of heat to the system is stopped, then

$$0 = (W.C_p + C.E.)\frac{dT_o}{d\theta} + \frac{dQ_L}{d\theta} \qquad (5\text{-}6)$$

then substituting 5-6 in Equation 5-5 we have

$$\frac{dQ}{d\theta} = (W.C_p + C.E.)\left(\frac{dT}{d\theta} - \frac{dT_o}{d\theta}\right) \qquad (5\text{-}7)$$

Specific heat of liquids may be calculated from Equation 5-7 knowing $\frac{dT}{d\theta}$, $\frac{dT_o}{do}$, W, C.E. and the rate of heat supply.

Apparatus:

A sketch of the calorimeter used for specific heat measurement is shown in Figure 5-1. It consists of an insulated glass beaker (250 ml) placed inside another insulated polythene beaker. There is covered by a 3 inch thick rubber stopper with a central hole for the heating device. Heating device consists of a porecelain rod would with nichrome wire (resistance = 16.30 Poreclain rod is sealed inside a test tube with a provision at the top for lead wires. A magnetic stirrer is used for mixing the beaker contents.

Electrical circuit consists of a variac connected in parallel to an a.c. voltmeter (0.30V) and in series to an a.c. ammeter (0-2.5 A). Temperature measurements were made with a copper constantan thermocouple and a potentiometer (Toshniwal) (0-17 mV). Power is supplied from the mains through the variac (voltage being nearly 16.0V and amerage nearly 1.0A). Temperature readings were accurate upto 0.005°C.

Procedure:

A known amount of black liquor sample was taken in the beaker and heated upto the required temperature by slow heating. Reducing the heat supply the temperature of the sample was maintained in the vicinity of the desired value for specific heat measurement for about 20 minutes to attain equilibrium conditions. The power supply was then turned off

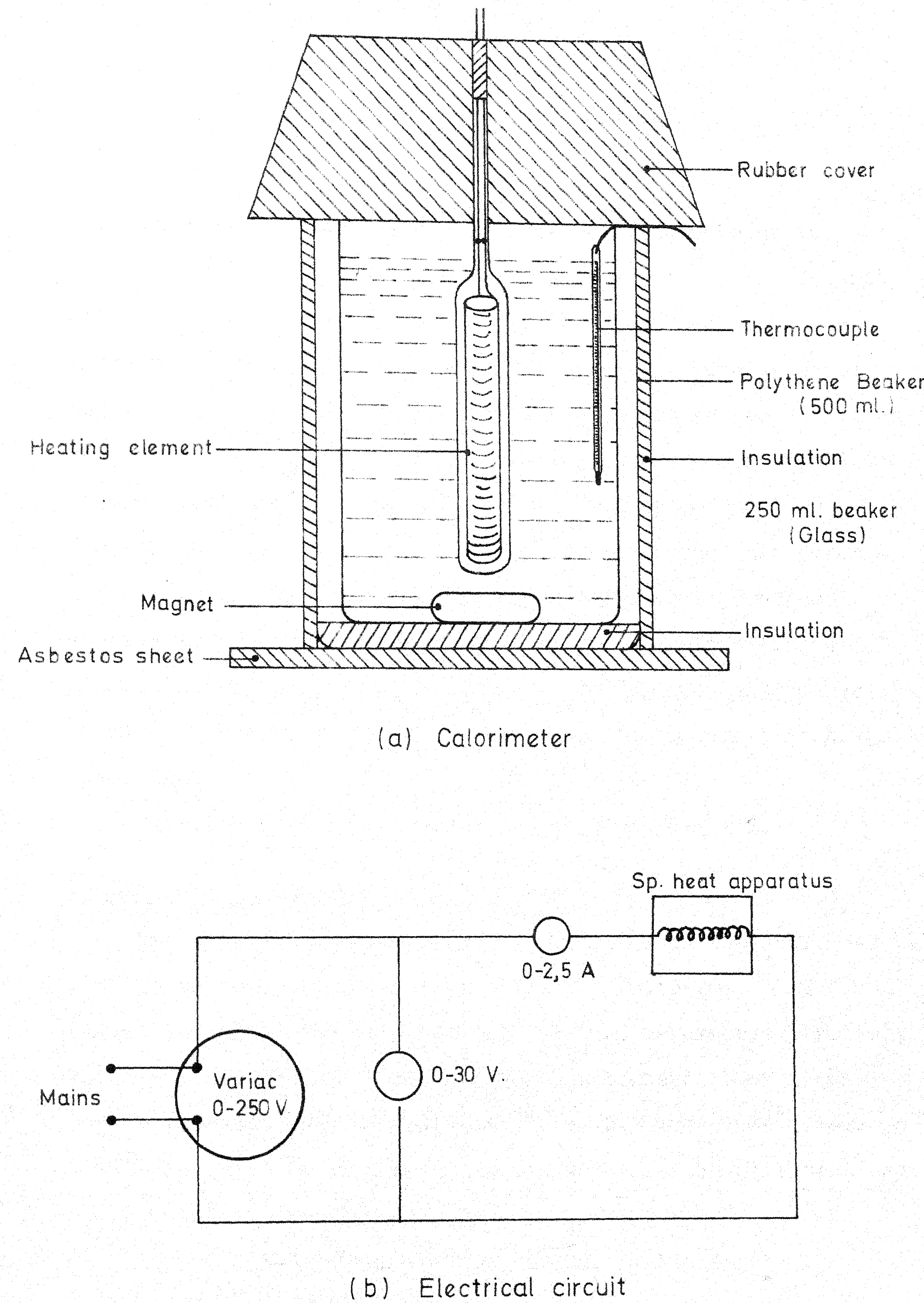


FIG. 5-1. Specific Heat Apparatus.

and readings of temperature were noted at intervals of two minutes until the temperature fell about 4°C below the desired value at which specific heat was to be determined. The the current was turned on and temperature readings were taken at the interval of two minutes until the temperature was 2°C above the desired temperature level. The experiment was repeated to obtain consistent values of slopes of cooling and heating curves. Loss of sample by evaporation during the experiment was determined by weighing the beaker contents. Magnetic stirrer is not efficient for use with viscous black liquor especially at higher concentration. Instead, the sample was diluted with a known amount of water and the specific heat was determined.

Sample calculations are presented in Appendix E.

Results and Discussions:

Experimental data and results are given in the Table 5-1 for the temperature range 50-80°C and concentration 15-50% solids. Figure 5-2 gives the graphical correlation of experimental data. The data show that the specific heat of bagasse black liquor varies linearly with concentration for the three temperature levels included in this work passing through 1.00 corresponding to 0.0% solids line (water).

Equation 5-8 represents the experimental data

$$C_p = (0.9930 - 0.01258\ c) + (.5555 \times 10^{-4} + .104 \times 10^{-3} c)T \tag{5-8}$$

The percentage error between the calculated values and the experimental data is less than 0.4%. This error can be reduced to less than 0.25% using Equation 5-9 with six constants.

$$C_p = (1.0461 - 0.01553\ c) - (.164080 \times 10^{-2} - .1956 \times 10^{-3} c)T + .1307 \times 10^{-4} - .72 \times 10^{-6} c)\ T^2 \qquad (5\text{-}9)$$

Equation 5-8 would be adequate for engineering calculations.

The graph shown in Figure 5-3 enable a comparison of the results of this work at 50°C with the results of the previous investigators based on Equations 5-1, 5-2, and 5-3.

From Figure 5-3 it is clear that the results of this work is in close agreement with Stevenson's equation near about 50°C. When the graphs are extrapolated to cut the 100% solids ordinate specific heat of black liquor solids was found to vary from 0.25 to 0.55 in the range of 50-80°C, unlike 0.43 to 0.50 of Harvin's data. This shows that specific heat of bagasse black liquor solids is more susceptible to temperature changes than pine black liquors solids.

The results of this work for bagasse black liquor are compared with the values for black liquor from mixed woods(15). The values for bagasse black liquor are higher by 5.1 to 18.00 percent than that of mixed woods for the concentration range of 15-54 percent solids.

The specific heat values for bagasse black liquor compiled in Table 5-2, based on Equation 5-8 may be used for process enthalpy calculations.

TABLE 5-1 EXPERIMENTAL DATA OF SPECIFIC HEAT FOR BAGASSE BLACK LIQUOR

% Solids	Temp., °C	Mass of Sample, gm.	Rate of Heating cal/min.	Rate of Temp.Change Heating °C/min.	Rate of Temp.Change Cooling °C/min.	Sp.Heat Kcal/g°C
15.50%	50	255.279	228	0.616	0.1785	0.878
	70	273.701	277	0.412	0.4870	0.910
	80	255.279	90	0.127	0.6875	0.928
26.00	50	259.662	172	0.433	0.1630	0.802
	65	259.662	160	0.227	0.310	0.844
	80	259.662	229	0.200	0.5600	0.882
50.00	50	62.066	222	0.556	0.2060	0.618
	65	62.066	228	0.428	0.625	0.700
	80	62.066	230	0.1418	0.625	0.772

TABLE 5-2: SPECIFIC HEAT OF BAGASSE BLACK LIQUOR

Temp., °C	% Solids				
	20	30	40	50	60
30	0.802	0.699	0.596	0.492	0.389
40	0.824	0.735	0.646	0.558	0.469
50	0.845	0.769	0.694	0.618	0.543
60	0.866	0.802	0.739	0.674	0.610
80	0.908	0.863	0.818	0.772	0.727
70	0.887	0.834	0.879	0.725	0.672
90	0.928	0.890	0.852	0.814	0.776
100	0.948	0.916	0.883	0.852	0.819

Based on Equation (5-8)

TABLE 5-3: COMPARISON OF SPECIFIC HEAT OF BLACK LIQUORS

%Solids	Temperature °C	Bagasse C_p cal/g,°C	Mixed woods[15] C_p cal/g.°C	% Difference
15.5000	95.0	0.954	0.890	-6.72
17.0577	102.0	0.966	0.878	-9.10
19.7780	92.3	0.940	0.873	-7.12
23.4410	82.0	0.900	0.856	-5.10
30.3800	56.3	0.788	0.830	+5.32
41.7307	117.0	0.90	0.740	-17.80
53.0650	102.0	0.86	0.724	-15.80

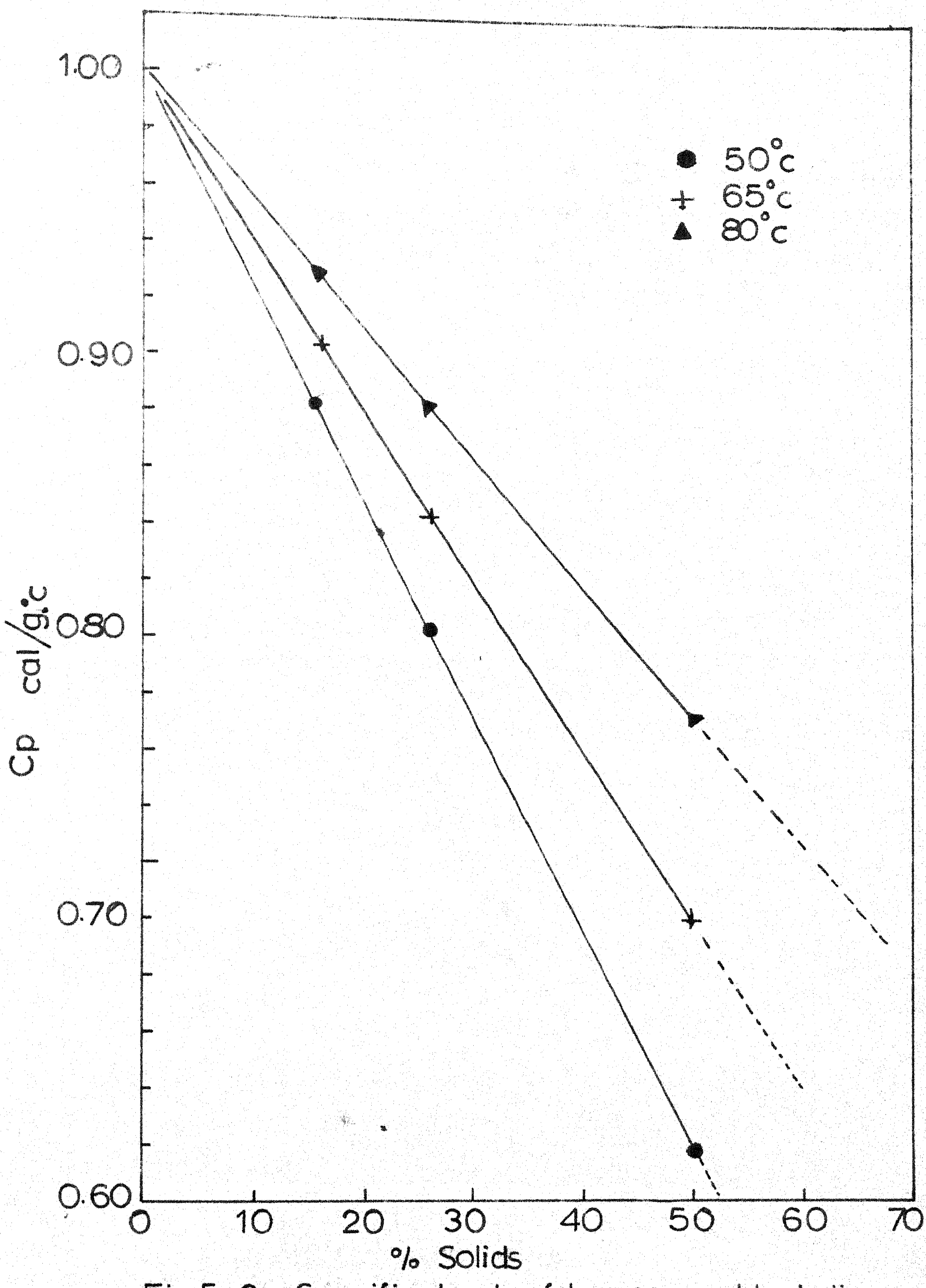


Fig.5-2 Specific heat of bagasse black liquor

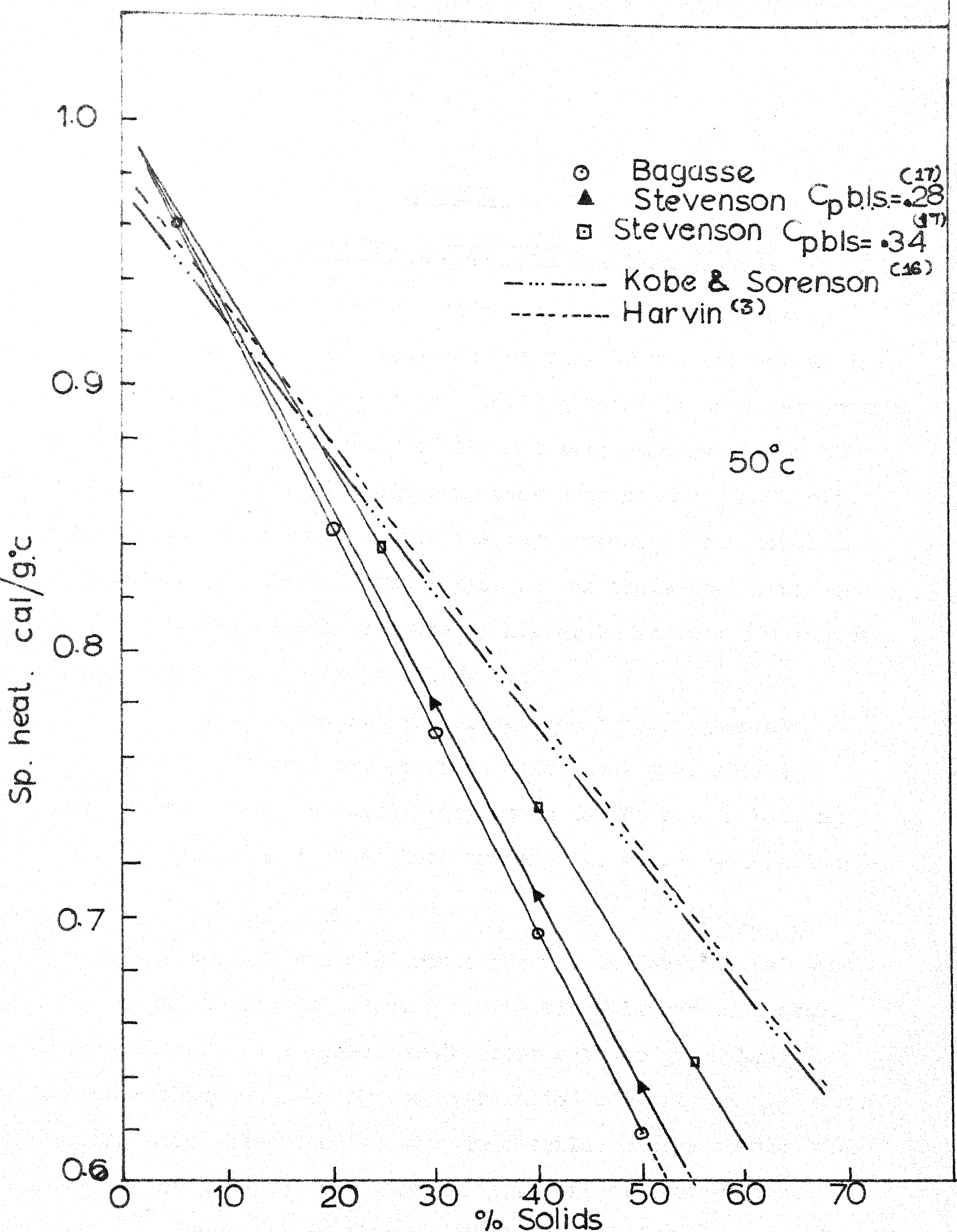


Fig. 5-3 Specific heat of black liquors

CHAPTER VI

BOILING POINT ELEVATION OF BLACK LIQUORS

Boiling point elevation is the difference between the boiling point of the solution and that of the solvent at the existing pressure of operation. Boiling point is that temperature at which the vapor pressure of the solution becomes equals to operating pressure. Certain compounds such as NaOH, NaCl etc. when dissolved in water reduce its vapor pressure and hence the temperature at which the vapor pressure of the solution becomes equal to the operating pressure is higher by an amount which is called the elevation of boiling point.

In evaporators, the elevation of boiling point decreases the temperature apparent difference available for heat transfer from the condensing steam to the liquor boiling inside tubes. The rate of heat transfer is given by Equation 6-1

$$Q = UA\,(\Delta T) \qquad (6\text{-}1)$$

The actual temperature difference for use in Equation 6-1 would include the boiling point rise of the black liquor processed. This would have the effect of decreasing the rate of heat transfer thereby lowering the evaporation capacity of the unit. Boiling point elevation is used in detailed energy balance and heat transfer calculations of multiple effect evaporators. Perry[23] gives the boiling point elevation of various simple compounds. Black liquors are known to exhibit boiling point rise behavior, which increases with the concentration

of the liquor processed[24]. Han[4] has observed the boiling point rise at various concentrations of neutral sulfide spent liquors and kraft black liquors.

In this work boiling point rise of bamboo and bagasse black liquors is determined at atmospheric pressure for the concentration range 15-54% solids, using a simple experimental set-up.

Results and Discussion:

Table 6-1 gives the values of the boiling points of bamboo and bagasse black liquors. These results are graphically presented in Figure 6-1 as the plot of Boiling point rise vs. percent solids concentration in the black liquors. As may be observed from the curves in Figure 6-1, the boiling point rise increases with concentration for both bamboo and bagasse black liquors. Boiling point rise of8and 10°C is obtained for 54% solids bagasse and bamboo black liquors respectively. This compares very well with the value of 8°C reported by Han[4] for 52% solids neutral sulfite spent liquors and kraft black liquors. The values obtained for bamboo black liquor are 13-35 percent higher than the corresponding values for bagasse black liquors over the concentration range 20-50 percent solids. Boiling point elevation data obtained in this work may be used for detailed heat transfer and energy balance calculations of multiple effect evaporators.

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TABLE 6-1: BOILING POINT ELEVATION OF BLACK LIQUORS

% Solids	B.P., °C	B.P.E °C
A. Bamboo Black Liquor:		
18.0	103.5	4.3
44.5	107.1	7.9
54.0	109.5	10.3
B. Bagasse Black Liquor:		
16.0	101.5	2.3
44.0	106.0	6.8
50.0	107.0	7.8

Atmospheric pressure = 738.5 mm Hg.

Boiling point of water = 99.2°C

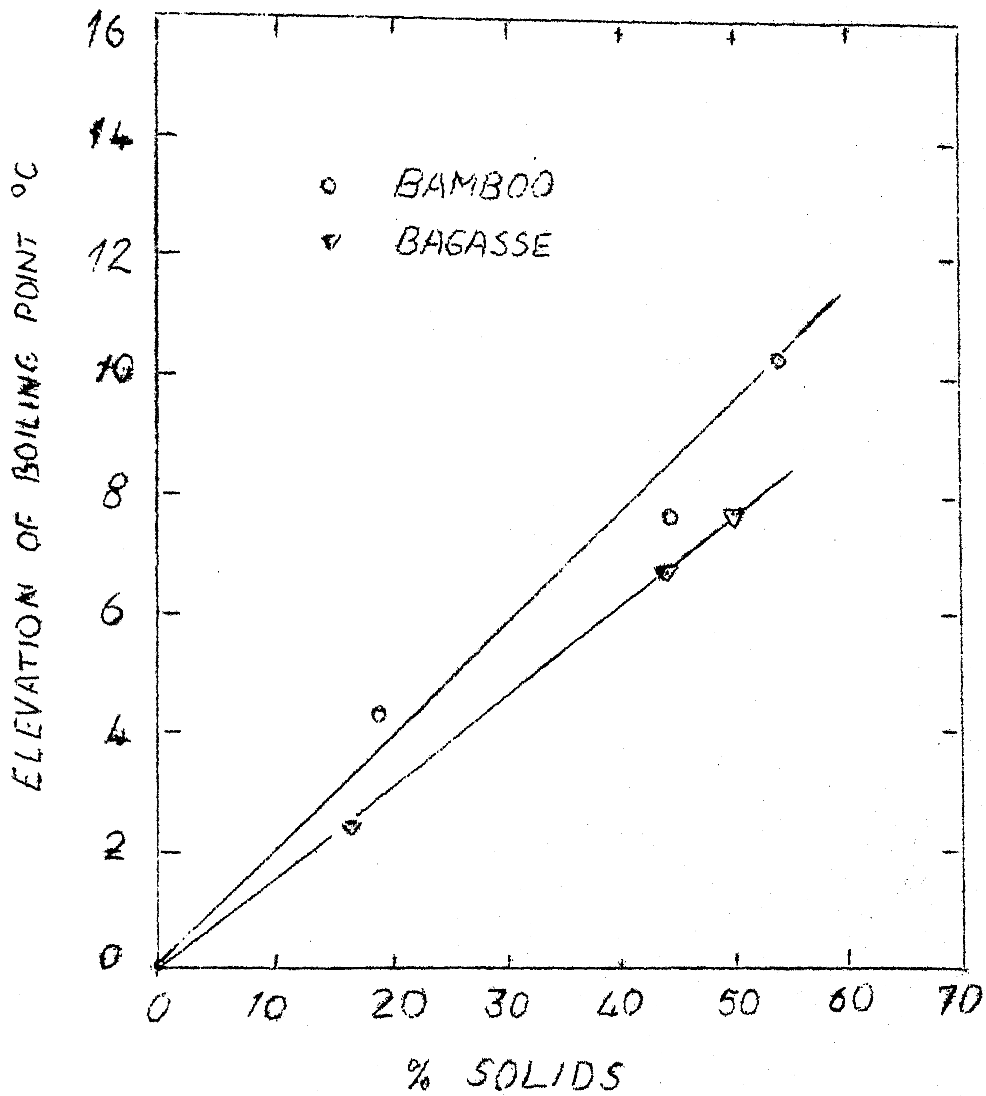

Fig 6-1 Boiling point elevation of black liquors

CHAPTER VII

SUMMARY

This investigation deals with the experimental measurement of engineering data, such as specific gravity, viscosity, thermal conductivity and boiling point elevation for various commercial black liquor samples, for the temperature range 30-95 °C and 15-55% solids concentration. The commercial black liquor samples were obtained from paper industries utilizing bamboo, bagasse, bamboo + salai, and eucalyptus as the fibrous raw materials for pulping.

1. Specific gravity of the black liquor varies linearly with temperature at a particular specific gravity data of all the black liquor samples of this work may be correlated well (less than 2.0 percent error) by equation 2-2.

$$s = (1.0104939 + 0.00755064c) + (-0.00043592 + 0.0000441c)T \tag{2-2}$$

2. Viscosity of the black liquors increase with a rise in concentration and decrease with an increase in temperature. An increase in temperature from 50 to 70°C decreases the viscosity of bamboo black liquor by 30% at 20% solids and by 90% at 50% solids concentration. The viscosity of 20% and 50% bamboo black liquor decrease by 25% and 66% of their values at 70°C as the liquor temperature increases to 90°C. Similar behavior is observed for bagasse, bamboo + salai (10%) and eucalyptus

black liquors. Bamboo and bagasse black liquors exhibit non-Newtonian behavior above 45 percent solids.

3. The thermal conductivity of bagasse and bamboo black liquors vary linearly with concentration for a given temperature level.

4. The specific heat of bagasse black liquor varies linearly with concentration at given temperature.

5. The boiling point elevation of bamboo and bagasse black liquors increase with liquor concentration.

The compilation of engineering data for black liquors obtained in this work would be useful for process calculations, selection and design of equipments for chemical recovery operations in a kraft pulp mill, process research and development work and scale up studies.

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APPENDIX A

SAMPLE CALCULATIONS
FOR VISCOSITY OF BLACK LIQUOR

a. Capillary Viscometer:

At 13.5 percent concentration of Bamboo sample

Efflux time = 202 sec.

Viscometer constant = 0.0122 c.s./sec.

Temperature = 24.8°C

ρ = Density at 248°C = 1.10 gm/cc

ν = Kinematic viscosity = kc x t

where kc = viscometer constant varies for different viscometer depending upon the diameter, length of capillary and volume of the liquid taken.

$$\nu = 0.0122 \times 202$$
$$= 2.4644 \text{ c.s.}$$
$$\eta = \text{viscosity in c.p.} = \nu \times \rho$$
$$= 2.46 \times 1.1 = 2.71084 \text{ c.p.}$$

Viscometer Constant was determined by calibrating the viscometer with water and glycerol solutions.

b. Stormer Viscometer: For bamboo sample of61.1 percent concentration at 86°C.

$$\eta = \frac{W \times t}{A} = k \times W \times t.$$

k = 0.0325 c.p./g.x sec. determined by standard glycerol solution

t = time in seconds for 100 revolutions

W = weight applied; t = time = 214 sec.; weight = 250 g.

Viscosity = 0.0325 x 250 x 214 = 1740 c.p.

APPENDIX B

SAMPLE CALCULATION FOR THERMAL CONDUCTIVITY

$x_1 = x_2 = x_3 = 0.00794$ m.

$x_l = x_U = 0.00318$ m.

$A_1 = 0.1268$ sq.cm. $= 0.01268$ sq.m.

$A_{21} = 0.01392$ sq. m. $\qquad A_{22} = 0.01425$

$A_3 = 0.01561$ sq.m.

$A_{12} = A_1 + A_2/2 = 0.01332 \qquad A_{23} = 0.01492$

Substituting these values with an assumption of $k_1 = k_2 = k_3$

$= 96.6$ kcal/hr.sq.m.°K/m.

in the equation (4-6), we have

$$\frac{\Delta T_{12}}{\Delta T_{23}} = \frac{0.00853 + 0.02375/k_U}{0.000760 + 0.0212/k_l}$$

Taking k_U and $k_l = .5$ kcal/hr.sq.m.°K/m. since the thermal conductivity value of water ranges from 0.4 to 0.6 kcal/hr.sq.m.°K/m. in the range of 30° to 100°C. We have

$$\frac{\Delta T_{12}}{\Delta T_{23}} = \frac{0.000853 + 0.0475}{0.000760 + 0.0424} = \frac{0.048353}{0.043160} = 1.112$$

By neglecting terms due to thermal conductivity of the metal also leads to

$$\frac{\Delta T_{12}}{\Delta T_{23}} = 1.122 \quad \frac{k_l}{k_U} \qquad \text{(B.1)}$$

That means, without much significant error in the calculation, Equation b-1 can be used for thermal conductivity calculation with this particular apparatus.

<u>Example</u>: Bagasse liquor at 50% concentration and at 50°C. Water was taken in the bottom tough

$E1 = 2.116$ $\qquad E12 = \frac{E1 + E2}{2} = 2.046$

$E2 = 1.97$

$E3 = 1.86$ $\qquad E23 = \frac{E2 + E3}{2} = 1.915$

T12 corresponding to E12 is 50.178°C

T23 corresponding to E23 is 47.092°C

Then k_1 = thermal conductivity of water at 47.092°C is

0.55 kcal/hr.sq.m °K/m.

$\Delta E12 = E1 - E2$

$\Delta E23 = E_2 - E_3$

Assuming $\frac{\Delta T12}{\Delta T23} = \frac{\Delta E12}{\Delta E23}$, and substitutting in the equation B-1 we have

$$k_U = 1.122 \times 0.55 \times \frac{0.11}{0.155}$$

$$= 0.43902 \text{ kcal/hr.sq.m °K/m.}$$

APPENDIX C

SAMPLE CALCULATION OF SPECIFIC HEAT OF BLACK LIQUOR

a. Determination of Calorimeter Equivalent:

Temperature = 50°C

W = 205.3940 gm.

Amperage = 0.78A

Voltage = 12.8V

Power factor = 0.98 assumed

$$\frac{dQ}{d\theta} = 14.35 \text{ V.I. } \cos \phi = 140 \text{ cal/min.}$$

Slopes from the graphs plotted for cooling and heating are

Average $\frac{dT}{d\theta} = 0.570$

Average $\frac{dT_o}{d\theta} = -0.375$

Specific heat of Toluene at 50°C = 0.42 cal/g.°C

$$\therefore \frac{dQ}{d\theta} = (W.C_p + C.E.) \left(\frac{dT}{d\theta} - \frac{dT_o}{d\theta}\right) \qquad (C-1)$$

Substituting we have C.E. = 63 cal/°C

b. Sample Calculation for black liquor at 50°C solids concentration.

Temperature = 50°C

From graph average $\frac{dT}{d\theta} = 0.556$°C/min.

average $\frac{dT_o}{d\theta} = -0.206$°C/min.

$W_b = 62.066$ g. $\qquad$ w = 188.580 g.

Amperage = 0.98 A $\qquad$ Voltage = 16.10V

$$\frac{dQ}{d\theta} = 14.35 \text{ VI } \cos \phi = 220 = 220.8 \text{ cal/min.}$$

Then substituting in the equation

$$\frac{dQ}{d\theta} = (W.C_{pB} + W.C_{pw} + C.E.) \left(\frac{dT}{d\theta} - \frac{dT_o}{d\theta}\right)$$

Specific heat of black liquor = 0.618 cal/g°C

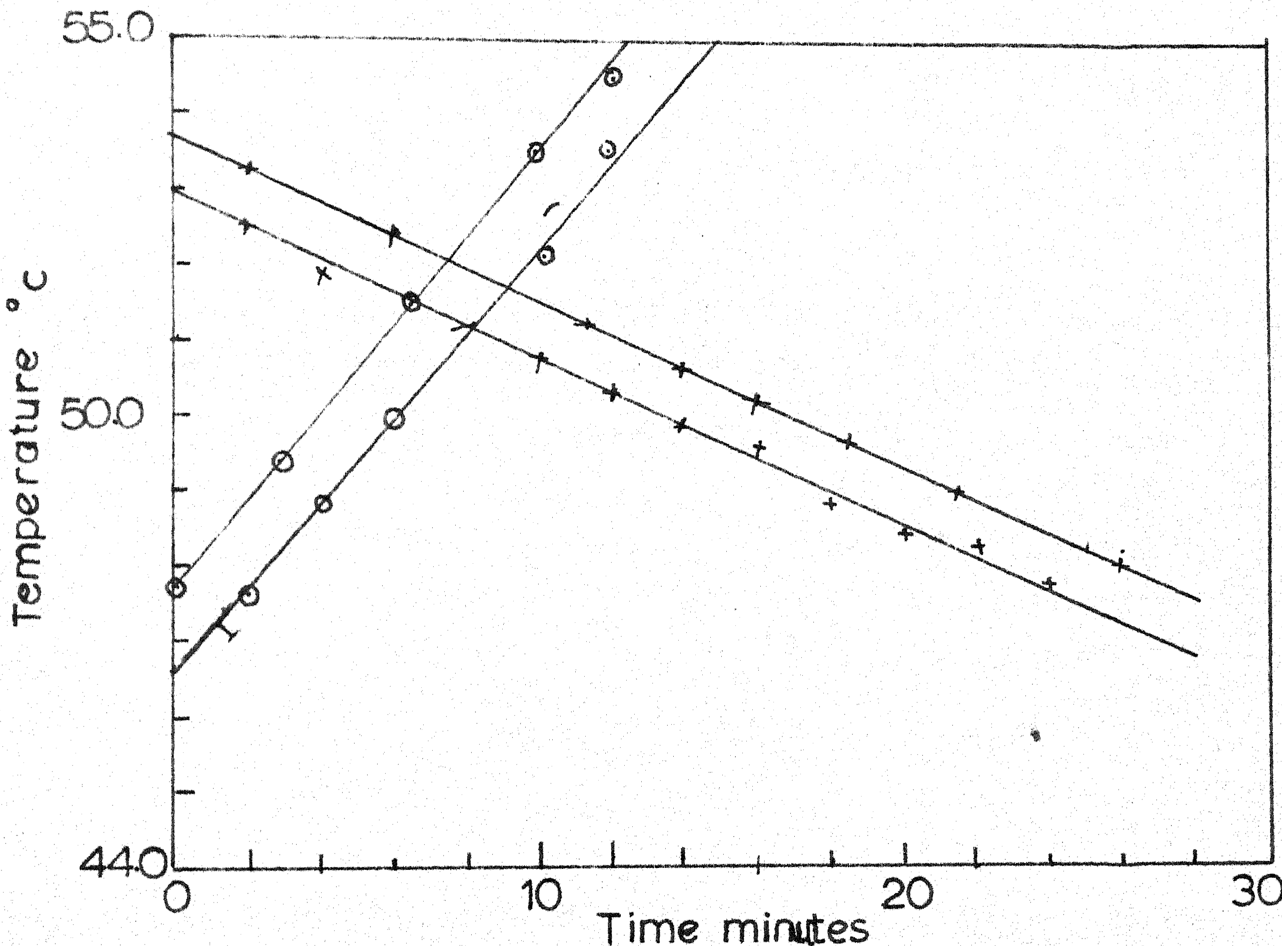

Fig. G-1 Heating & cooling curves of bagasse black liquor (50 % Solids)